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16. Abstracts   A method of modifying the surface of materials for use in prosthetic devices in contact with blood has been developed by the deposition of glow discharge polymer. The effect of choice of monomer and of operational parameters on the chemical nature of the glow discharge polymer has been extensively elucidated. Good reproducibility has been demonstrated and tests by other contractors have indicated promising blood compatibility. The method therefore yields a very thin (50-1000 A), highly adhesive and cohesive coating that does not affect the bulk properties of the substrate. Surfaces with a wide range of chemical properties are accessible by this technique. In the last year of the project a barrier to leaching of plasticizer from poly(vinyl chloride) has been formed by glow discharge treatment and a change of chemical properties for tetramethyldisiloxane glow discharge polymer has been found with aging.

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FORWARD

A study of electrodeless glow discharge as a means of modifying the surface of polymers was initiated under our contract No. NIH-NO1-HB-3-2913 in November 1972. This final report consists of two major parts; i.e., 1) The overall summary of the project in the period of 1972 - 1979, and 2) annual report to cover the research activities in our final period December 1978 through November 1979.

The contract was initiated by Dr. H. Yasuda who served as principal investigator until 1978. It continued under the direction of Dr. N. Morosoff at the Research Triangle Institute when Dr. Yasuda moved to the University of Missouri-Rolla in 1978. During the 1978-1979 period, Dr. Yasuda served as coprincipal investigator and was responsible for a portion of the contract tasks, notably the preparation of samples for biological testing by other contractors. Because of the historic background of the contract, the overall review of the project is written by Dr. Yasuda; Dr. Morosoff has summarized the results of the final year and both investigators have contributed to the Conclusions.

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1.0 Overall Review of the Project

1.1 Introduction

When this project was initiated, it was known that the exposure of a polymer to a glow discharge atmosphere will modify the surface of the polymer, known as CASING (Crosslinking by Activated Species of Inert Gases), indicating glow discharge treatment of a polymer can be used in the modification of a polymer surface. It was also known that glow discharge of an organic material (monomer) will lead to the formation of polymeric materials and often leads to a thin layer of coating onto the surface of a substrate exposed to such a glow discharge.

We had a certain knowledge of this aspect, namely glow discharge polymerization, owing to our previous experience in our attempt to prepare ultrathin membranes by this technique.

Accordingly, our initial efforts were aimed at both glow discharge treatment of polymer surfaces by nonpolymer-forming glow discharge, and the modification via the application of ultrathin coating by glow discharge polymerization. However, it soon became evident that the change or modification of surface characteristics obtained by treatment with nonpolymer-forming glow discharge, such as argon or nitrogen, without application of ultrathin film, decay with time after the treatment although a permanent modification is effected. Contrary to this, it was quite evident that the application of ultrathin layer by glow discharge polymerization provided a much more stable modification. Because of this time dependent characteristic, or the decay of modification effects, the major emphasis of the project in the later years was shifted to the method which relies upon the laying-down of ultrathin coating by glow discharge polymerization.

It is regrettable that this situation has been mistaken or mis-quoted in some reports and review articles as if the modification obtained by the glow discharge polymerization was not a long lasting one. Contrary to this misquotation, glow discharge polymerization provides most stable surfaces known today.

Although we had certain knowledge on glow discharge polymerization and there also were numerous reports which support the potential of the method, as far as the fundamental aspects of polymer formation were

concerned, no clean-cut view was available at that time. Consequently,
it was necessary to carry out a certain amount of fundamental studies to
elucidate the mechanisms of polymer formation in order to obtain the
surfaces which will be suitable for modification of biomaterial surfaces.
This aspect of the study is summarized in Sections 2 and 3.

In order to provide a general picture on the current art of the
subject, i.e. glow discharge polymerization or coating, the report is
presented in a form of review including work appearing in literature
during this reporting period, rather than summarizing the experimental
results in a chronological order.

1.2 Glow Discharge Polymerization Processes

When an organic vapor is injected into a glow discharge of an inert
gas such as argon, or when a glow discharge of a pure organic vapor is
created, the deposition of polymeric films onto an exposed surface is
often observed. Polymer formation that occurs in such a process is
generally referred to as plasma polymerization or glow discharge poly-
merization.

The recognition of thin film formation by glow discharge polymeri-
zation can be traced back to 1874.[1,2] However, in most cases the polymers
were considered as byproducts of an electric discharge[3-9] and, conse-
quently, little attention was paid either to the properties of those
polymers (undesirable byproducts) or to the process as a means of forming
polymers.

Only in relatively recent years (about the 1950's) has glow discharge
been utilized in a practical way to make a special coating on metals.
Once some of the advantageous features of plasma coating (e.g., flawless
thin coatings, good adhesion to the substrate, chemical inertness, and
low dielectric constant) were recognized, much applied research on the
use of the process was done. The literature cited here[15-63] represents
only some of the early investigations.

In order to distinguish the term plasma polymerization, which is
used to describe a special kind of polymer formation mechanisms in glow
discharge, the term glow discharge polymerization is used in this report
to refer to plasma polymerization in the wider meaning. Therefore, in
the context used in this report, plasma polymerization refers to polymer-

ization mechanisms that constitute a portion of the glow discharge polymerization.

1.2.1 Characteristic Aspects of Glow Discharge Polymerization

1.2.1.1 Glow Discharge Polymerization

Although the phenomemon of polymer formation in a glow discharge is referred to as glow discharge polymerization, the terminology of polymerization may not represent the actual process of forming a polymer, or the word "polymerization" may even be misleading. The conventional meaning of polymerization is that the molecular units (monomers) are linked together by the polymerization process. Therefore, the resultant polymer is conventionally named by "poly + (the monomer)". For instance, the polymer formed by the polymerization of styrene is named polystyrene. In this conventional context, polymerization refers to molecular polymerization--i.e., the process of linking molecules of a monomer.

In a strict sense, polymerization in the conventional context does not represent the process of polymer formation that occurs in a glow discharge--although such polymerization may play a role, depending on the chemical structure of a monomer and also on the conditions of the glow discharge.

In contrast to conventional polymerization--i.e., molecular polymerization--polymer formation in glow dicharge may be characterized as elemental or atomic polymerization. That is, in glow discharge polymerization, the molecular structure of a monomer is not retained, and the original monomer molecules serve as the source of elements which will be used in the construction of large molecules. Therefore, glow discharge polymerized styrene is not polystyrene. Also, glow discharge polymerized benzene is not polybenzene, but glow discharge polymers of styrene and of benzene are very much alike.

Because of this characteristic nature of the polymer formation process, the starting compound cannot be considered to be the monomer in the conventional context used in relation to the corresponding polymer. A compound used in glow discharge polymerization is merely a starting material in the process.

A polymer formed by glow discharge polymerization cannot be identified by the starting material since the molecular structure of the

starting material is not retained in the polymer structure. This leads
to another important point--that glow discharge polymerization or polymers
formed by glow discharge of a starting material are highly dependent on
the system or conditions under which the polymer is formed.

In other words, glow discharge polymerized styrene is not polysty-
rene, and there is no material that can be fully identified as glow
discharge polymerized styrene. Not enough emphasis has been placed on
the latter aspect, perhaps due to the somewhat misleading use of the
word polymerization, and also due to an a priori concept of polymerization
and lack of the distinction mentioned above.

It should be noted here that a polymer similar to polystyrene can
be formed by using an electric discharge process if conditions are
chosen to favor conventional polymerization of styrene. Even in such a
case, the polymer that is formed is generally not quite equivalent to
the conventional polystyrene because polymer formation that is charac-
terized by atomic polymerization usually occurs simultaneously. The
balance between different polymer formation mechanisms is indeed an
important factor which contributes to the system-dependent nature of
glow discharge polymerization.

1.2.1.2 Overall Mechanism of Polymer Formation in Glow Discharge

The individual steps or reactions that are involved in the process
of polymer formation in a glow discharge are extremely complex; however,
several important types of phenomena can be identified in order to
construct a general picture of glow discharge polymerization. The
process involved can be represented schematically as in Figure 1.[70]
Glow discharge polymerization can be considered to consist of two major
types of polymerization mechanisms. The direct route is plasma-induced
polymerization and another is plasma polymerization. Plasma-induced
polymerization is essentially the conventional (molecular) polymerization
triggered by a reactive species that is created in an electric discharge.
In order to form polymers by plasma-induced polymerization, the starting
material must contain polymerizable structures such as olefinic double
bonds, triple bonds, or cyclic structures.

Plasma (atomic) polymerization is a unique process which occurs
only in a plasma state. This polymerization can be represented by:

CAP (COMPETITIVE ABLATION AND POLYMERIZATION)
SCHEME OF GLOW DISCHARGE POLYMERIZATION
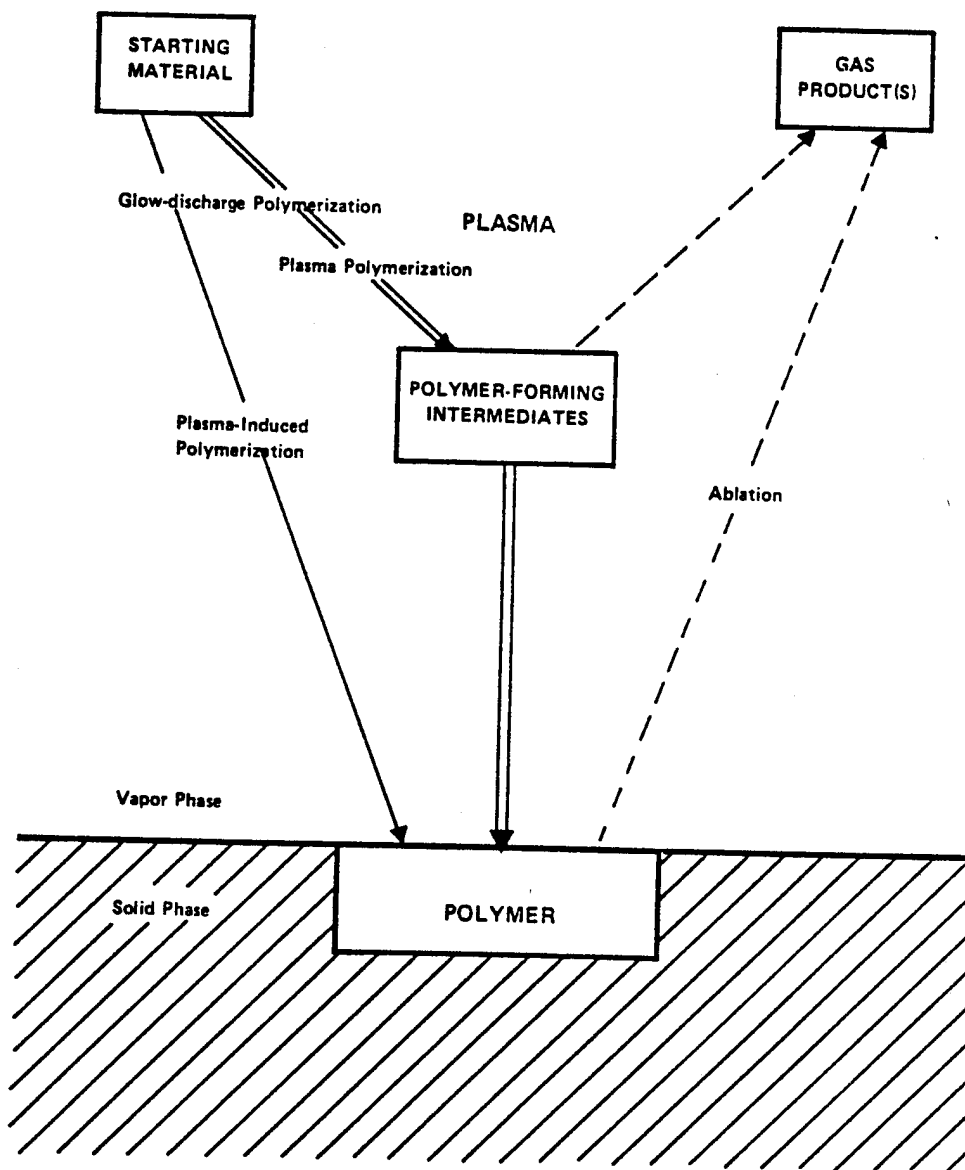
Figure 1. Overall mechanism of glow discharge polymerization.

Initiation or Re-initiation

$$M_i \rightarrow M_i^*$$
$$M_k \rightarrow M_k^*$$
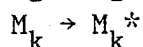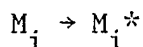
Propagation and Termination

$$M_i^* + M_k^* \rightarrow M_i\text{-}M_k$$
$$M_i^* + M_k \rightarrow M_i\text{-}M_k$$
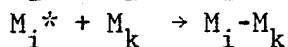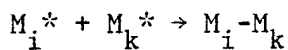
where i and k are the numbers of repeating units (i.e, i = k = 1 for the
starting material), and M* represents reactive species which can be an
ion of either charge, an excited molecule, or a free radical, produced
from M but not necessarily retaining the molecular structure of the
starting material (i.e., M can be a fragment, or even an atom detached
from the original starting material).

In plasma polymerization, the polymer is formed by the repeated
stepwise reaction described above. It should be noted that plasma-
induced polymerization does not produce a gas phase by product, since
the polymerization proceeds via utilization of polymerizable structure.
Plasma-induced polymerization may be schematically represented by a
chain propagation mechanism as follows:
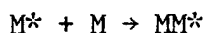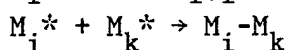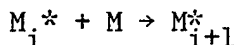
$$M^* + M \rightarrow MM^* \qquad \text{Propagation}$$
$$M_i^* + M \rightarrow M_{i+1}^*$$
$$M_i^* + M_k^* \rightarrow M_i\text{-}M_k \qquad \text{Termination}$$

It should be emphasized that general polymerization in a glow
discharge consists of both plasma-induced polymerization and plasma
polymerization. Which one of these two polymerization mechanisms plays
the predominant role in the polymer formation in a glow discharge is
dependent not only on the chemical structure of the starting materials,
but also on the conditions of the discharge.

Nonpolymer-forming gas products are produced in the process of
forming reactive (polymer-forming) intermediates and also in the process
of decomposition (etching) of the polymer deposit or of the substrate
material. Since polymer-forming species do not stay in the gas (plasma)
phase long enough, the major portion of the gas phase of a polymer-forming
glow discharge consists of the product gas, when a high conversion
ratio of a starting material to a polymer is obtained. This is an

extremely important factor; however, it has been dealt with lightly or has been completely neglected in most work appearing in the literature.

The characteristics of the product-gas plasma play the predominant factor in determining the extent of the ablation process, which is shown in Figure 1. Since the majority of work on glow discharge polymerization appearing in the literature is with hydrocarbons--which produce hydrogen as the product gas--the effect of ablation happened not to be great. Consequently, the complete neglect of ablation did not make a significnat difference in the overall picture of glow discharge polymerization. However, when a fluorine- ot oxygen-containing compound is used as the starting material, the image of glow discharge polymerization that is built around that of hydrocarbons is completely shattered. With such a compound as the starting material, the extent of ablation becomes the predominant factor, and the extent of polymer formation is entirely dependent on the extent of the product gas formation.

Perhaps the most dramatic demonstration of the ablation effect has been recently shown by Kay et al.[71] for glow discharge polymerization of CF_4. It had been thought that CF_4 was one of the very few organic compounds that does not polymerize in glow discharge. On the other hand, CF_4 has been used as one of most effect gases in plasma etching. Kay et al. have observed that no polymer deposition occurs under normal conditions in spite of the fact that C-F bonds are broken in the glow discharge, which is confirmed by mass-spectroscopic analysis of the gas phase. However, when a small amount of hydrogen is introduced into the discharge, deposition of polymer is observed. When the hydrogen flow is stopped, ablation of the polymer deposit occurs.

The situation observed in the above example may be visualized by the comparison of bond energies shown in Table 1. It should be noted that the energy level involved in a glow discharge is high enough to break any bond[72,73] (i.e., C-F is also broken although C-F is stronger than C-H). The important point is the stability of the product gas. The bond energy for F-F is only 37 kcal/mol, whereas H-F is 135 kcal/mol which is higher than 102 kcal/mol for C-F bond. The introduction of H_2 into the monomer flow evidently produces HF and removes F from the discharge system, thus reducing the etching effect by F_2 plasma. Although

Table I. Comparison of Bond Energies.

Bond	Energy, kcal/mol
C–C	80
C=C	142
C≡C	186
C–H	99
C–F	102
H–H	104
F–F	37
H–F	135

the term F_2 plasma is used to describe the effect of detached F in plasma, F_2 is not detected in the plasma state, perhaps due to its extremely high reactivity.[74]

It is interesting to note that F and O are two elements which reduce the rate of polymer formation from compounds that contain one of these elements. These two elements are the two most electronegative elements among all elements. Of course the bond energy itself is not a measure of the etching effect of plasma. For instance, the N-N bond is only 32 kcal/mol. However, N_2 plasma does not etch polymer surfaces; instead, the incorporation of N into the surface predominates.[75] Nevertheless, the importance of the ablation process shown in Figure 1 seems to be well demonstrated by the poor polymer formation in glow discharge polymerization of CF_4 and of oxygen-containing compounds.[76]

The polymer formation and properties of polymers formed by glow discharge polymerization are controlled by the balance among plasma-induced polymerization, plasma polymerization, and ablation; i.e., polymer formation is a part of the Competitive Ablation and Polymerization (CAP) scheme shown in Figure 1. The kind of conditions that affect these balances will be explained in the following section. Because of this CAP scheme of glow discharge polymerization, gas evolved from substrate materials also plays an important role particularly at the early stage of coating.

1.2.2 Processing Factors of Glow Discharge Polymerization

It is extremely important to recognize the difference between polymer-forming plasmas and nonpolymer-forming plasmas in order to understand the true meaning of the processing factors of glow discharge polymerization. Not all glow discharges yield polymer deposition. For instance, plasmas of Ar, Ne, O_2, N_2, and air are typical nonpolymer-forming plasma. The significance of polymer-forming plasmas, such as glow discharges of acetylene, ethylene, styrene, benzene, etc., is that a considerable portion or the majority of molecules of starting material leave the gas (plasma) phase and deposit as a solid polymer.

In contrast to polymer-forming plasmas, the total number of gas phase molecules in nonpolymer-forming plasmas do not change. Only a portion of gas molecules are repeating the process of being ionized,

excited, and quenched. However, the total number of gas molecules remains constant. This situation can be visualized by the pressure change that occurs before, during, and after the glow discharge. In the case of a nonpolymer-forming plasma, no pressure change is observed unless a material which reacts with excited species of plasma is placed in the discharge system.[77,78] The system pressure of a polymer-forming plasma changes as soon as discharge is initiated. The pressure change is dependent on the characteristic nature of the starting material, which is related to the product gas formation described in the previous section. With starting materials that yield very little product gas (e.g., acetylene, benzene, styrene, etc.) the system pressure drops to nearly zero when a high polymerization yield is obtained. In other words, an efficient plasma polymerization is an excellent vacuum pump, whereas a nonpolymer-forming plasma has no characteristic of this nature.

Unfortunately, most fundamental work on the plasma state was done with nonpolymer-forming plasmas, and the concept of the operational parameters used in such studies cannot be applied directly to polymer-forming plasmas.

Characteristic polymer deposition by glow discharge polymerization occurs onto surfaces exposed to (directly contacting) the glow. Some deposition of polymer, occurs on surfaces in nonglow regions(but the deposition rate is orders of magnitude smaller). The surface on which a polymer deposits could be an electrode surface, a wall surface, or a substrate surface suspended in the glow region. Another important factor that must be considered in dealing with operational factors of glow discharge polymerization is that glow discharge polymerization is system dependent. Consequently, polymer deposition rates are dependent on the ratio of surface to volume of glow. Therefore, other operational parameters such as flow rate, system pressure, and discharge power are insufficient parameters for the complete description of glow discharge polymerization. Such parameters serve as empirical means of describing operational conditions of glow discharge polymerization in a particular system, but they should not be taken beyond this limitation.

The following operational factors are important; however, all factors influence glow discharge polymerization in an interrelated

manner. Therefore, any single factor cannot be taken as an independent variable of the process.

1.2.2.1 Modes of Electric Discharge

Electric power sources with a frequency ranging between 0 (dc) and GHz (microwave) can be used for glow discharge polymerization. The use of a low frequency electric power source (up to about audio frequency range) requires internal electrodes. With higher frequency, external electrodes or a coil also can be used. Typical combinations of discharge modes and reactor design are shown schematically in Figure 2.

The use of internal electrodes has the advantage that any frequency can be used. The glow discharge is more or less restricted to the space between electrodes. The best glow discharge is obtained with internal electrodes at a relatively high pressure (> 0.1 torr). At lower pressure, the glow discharge expands beyond the space between electrodes. At low pressure (<0.02 torr) the glow occurs mainly in the space outside of the gap between the electrodes, and the system becomes inefficient for glow discharge polymerization. In order to restrict the glow to the space between the electrodes in the low pressure range, it is necessary to employ magnetic enhancement. Under typical conditions, polymer deposition occurs mainly onto the electrode surface. With a high frequency (rf range) power source, the glow tends to stray away from the space between the electrodes; however, because of this tendency polymer deposition onto a substrate surface placed in between the electrodes increases.[79]

The systems that employ external electrodes or a coil are suited for large volume glow discharges. They are particularly suited for the utilization of the tail-flame portion of the glow discharge. The tail-flame refers to the glow discharge away from the energy input region (under external electrodes or coil).

Whether a substrate is placed in the energy input region or placed in the tail-flame--or in the case of an internal electrodes system, whether a substrate is placed directly onto the electrode surface or placed in between electrodes--plays an important role in the properties of the polymer formed.[70,79-82] The relative location of the energy input and the polymer deposition is an important factor to be considered in view of the CAP scheme of glow discharge polymerization (Figure 1) in

(I)

(II)

(III)

(IV)
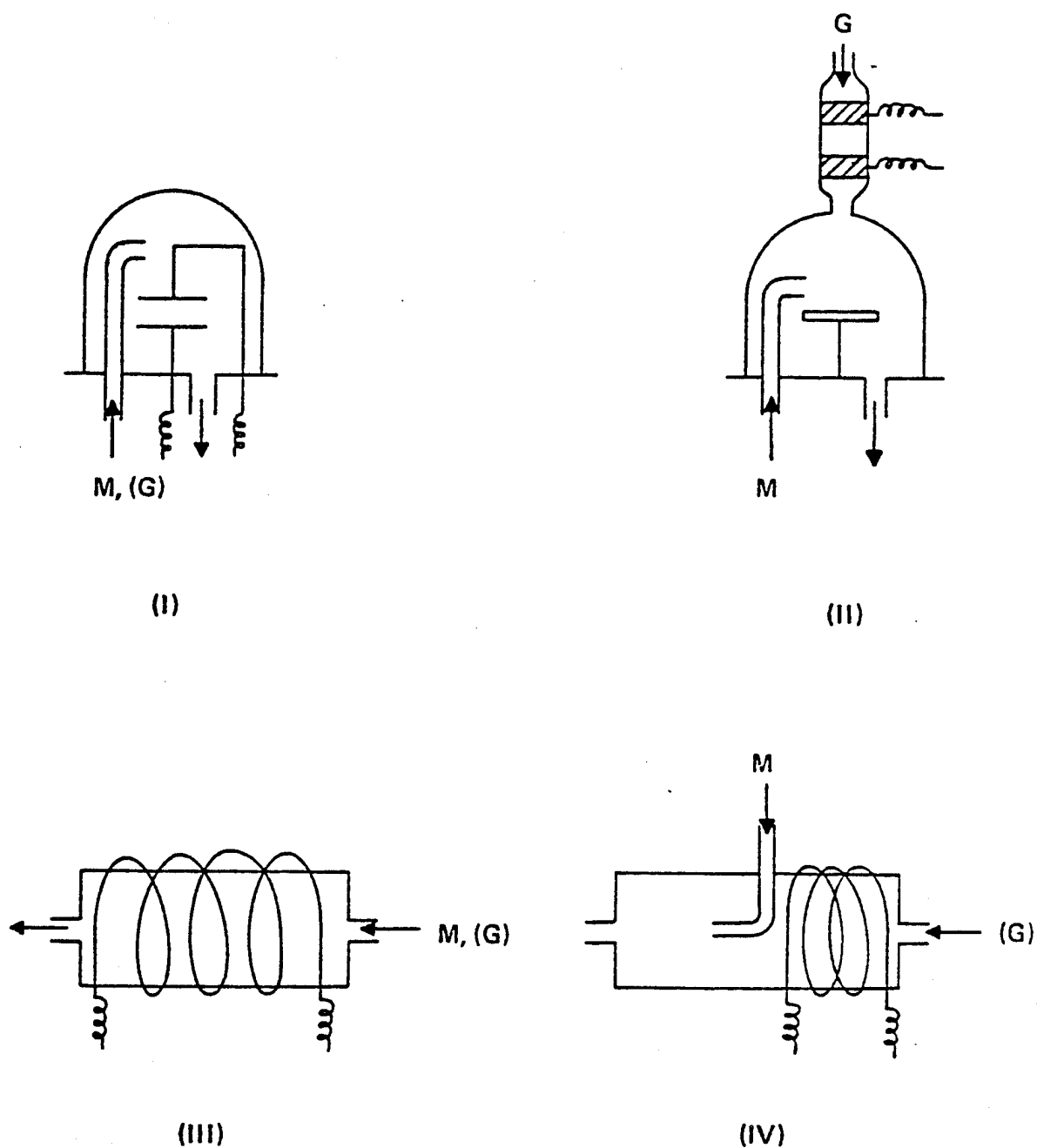
Figure 2.   Schematic representation of some typical arrangements of electric
discharge, flow of starting material, M, (and carrier gas, G), and
the location of polymer deposition.

which the substrate material also plays an important role in glow dis-
charge polymerization.

1.2.2.2 Flow Rate

The flow rate in most cases of glow discharge polymerization simply
refers to the feeding-in rate of the starting materials into the total
vacuum system and it does not necessarily mean the rate at which the
starting material is fed to the region of the system where polymerization
occurs.

It should be pointed out also that flow rates of a gas in a vacuum
system merely represent the total flux of gas but do not represent the
velocity of molecules as visualized in the flow of a liquid. The para-
meter F/p (where F is flow in cm^3(STP)/min, and p is the system pressure
in atm) is proportional to the velocity of gas molecules in a given flow
rate F at pressure p.

1.2.2.3 System Pressure

The system pressure is perhaps the most misunderstood and ill-treated
parameter of glow discharge polymerization. This misunderstanding or
mistreatment largely stems from the lack of distinction between nonpolymer-
forming and polymer-forming plasmas. As mentioned earlier, efficient
glow discharge polymerization is an excellent pump. Consequently, the
polymerization itself changes the system pressure. Another factor
contributing to the misunderstanding is the failure to recognize the
effect of product gas. In many cases, the system pressure observed
before glow discharge p_o is cited as though it represents the system
pressure during glow discharge polymerization, p_g. Some authors claim
that p_g is adjusted to p_o by controlling the pumping rate. Since p_g is
dependent on the production rate of product gas, such an operation is
not always possible. Furthermore, in view of the ablation process,
which is highly dependent on the amount of product gas, such an operation
does not seem to have any advantages or significance in controlling the
process.

The following points may clarify the meaning of system pressure in
glow discharge polymerization.

1. The system pressure before glow discharge, p_o, at a given flow
rate is entirely dependent on the pumping rate.[83] The higher the pumping
rate, the lower is the value of p_o.

2. The pumping rate of a system is dependent on the nature of the gas and is particularly important when a liquid nitrogen trap or a turbo-molecular pump is employed in a vacuum system as shown in Figure 3. These are excellent pumps for most organic vapors (starting material of glow discharge polymerization) and some gases; however, they offer virtually no pumping action for H_2, which is the main product gas when hydrogen-containing compounds are used as the starting material.

3. As far as the gas phase is concerned, glow discharge polymerization acts as an additional pump.

4. Glow discharge polymerization changes the gas phase from the starting material to the product gas.

5. Consequently, the system pressure with the glow discharge on, p_g, is largely determined by the pumping efficiency of the product gas, the efficiency of the polymerization, and the production rate of gas.

6. Therefore, there is no unique relationship between p_o and p_g. In a system where the polymerization yield is maintained at nearly 100 percent, p_g is determined by the flow rate but not by the value of p_o, as shown in Figure 4.

Since the velocity of gas molecules is dependent on pressure, the value of p_g (but not p_o) is important in controlling the distribution of polymer deposition and the properties of polymers formed in glow discharge polymerization; however, p_g cannot be considered as a manipulatable processing factor. The value of p_g can be manipulated to a certain extent, but it is largely determined by the nature of the starting material (i.e., gas production rate).

1.2.2.4 Discharge Power

The significance of discharge power in glow discharge polymerization is quite different from that for nonpolymer-forming plasmas. In essence, (the absolute value of) discharge power itself cannot be considered as an independent variable of the operation since a certain level of discharge power (e.g., 60 W) in a given set of discharge conditions for one starting material (e.g., ethylene) could not even initiate a glow discharge with another starting material (e.g., n-hexane) under otherwise identical conditions. In other words, a relative level of discharge power which varies according to the characteristics of starting materials
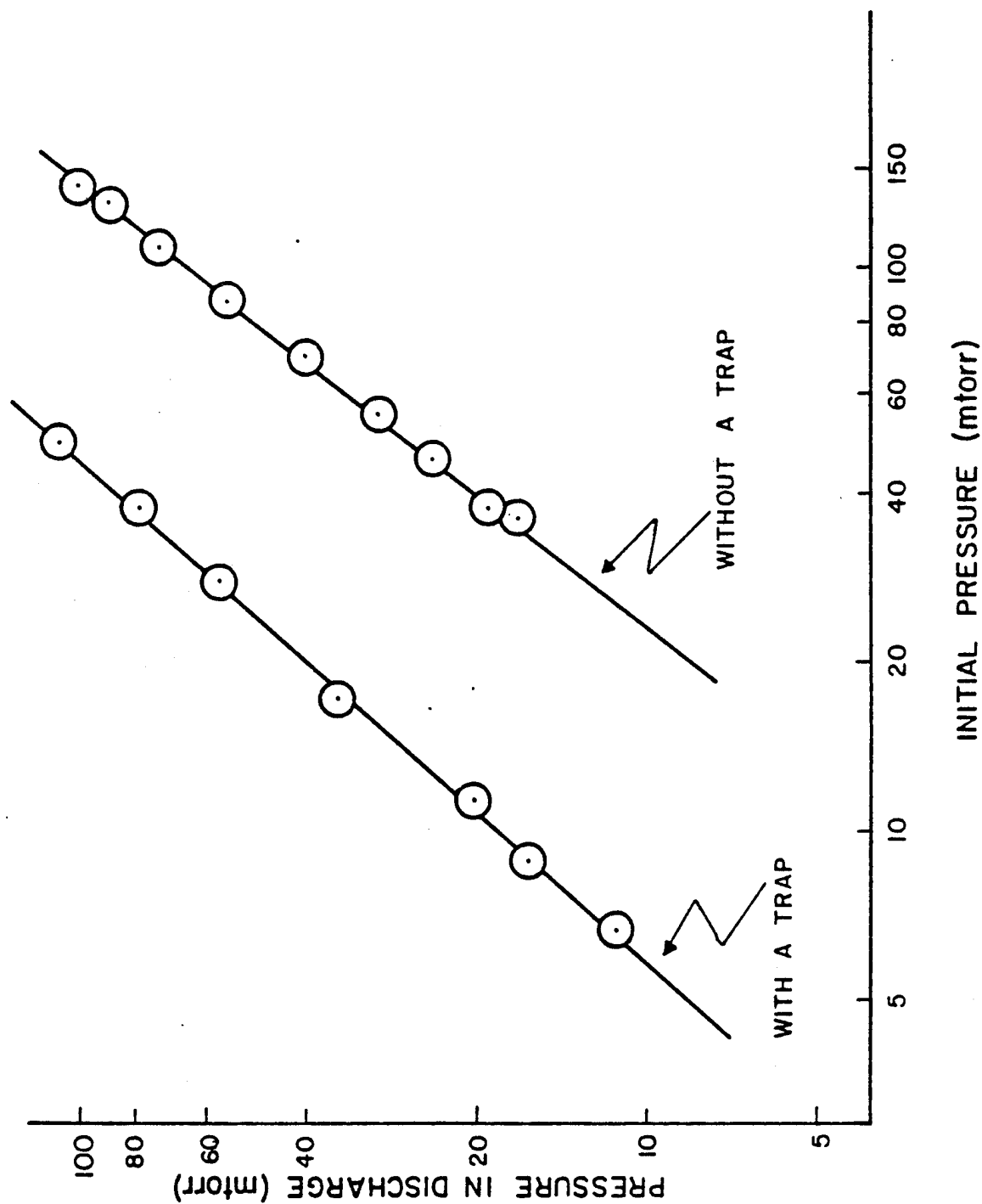
Figure 3. The dependence of system pressure in the discharge p_g on the initial system pressure p_o, for glow discharge polymerization of ethylene. The initial pressure at a given flow rate is dependent on the pumping rate of the system as shown by the two lines representing systems with and without liquid nitrogen traps.
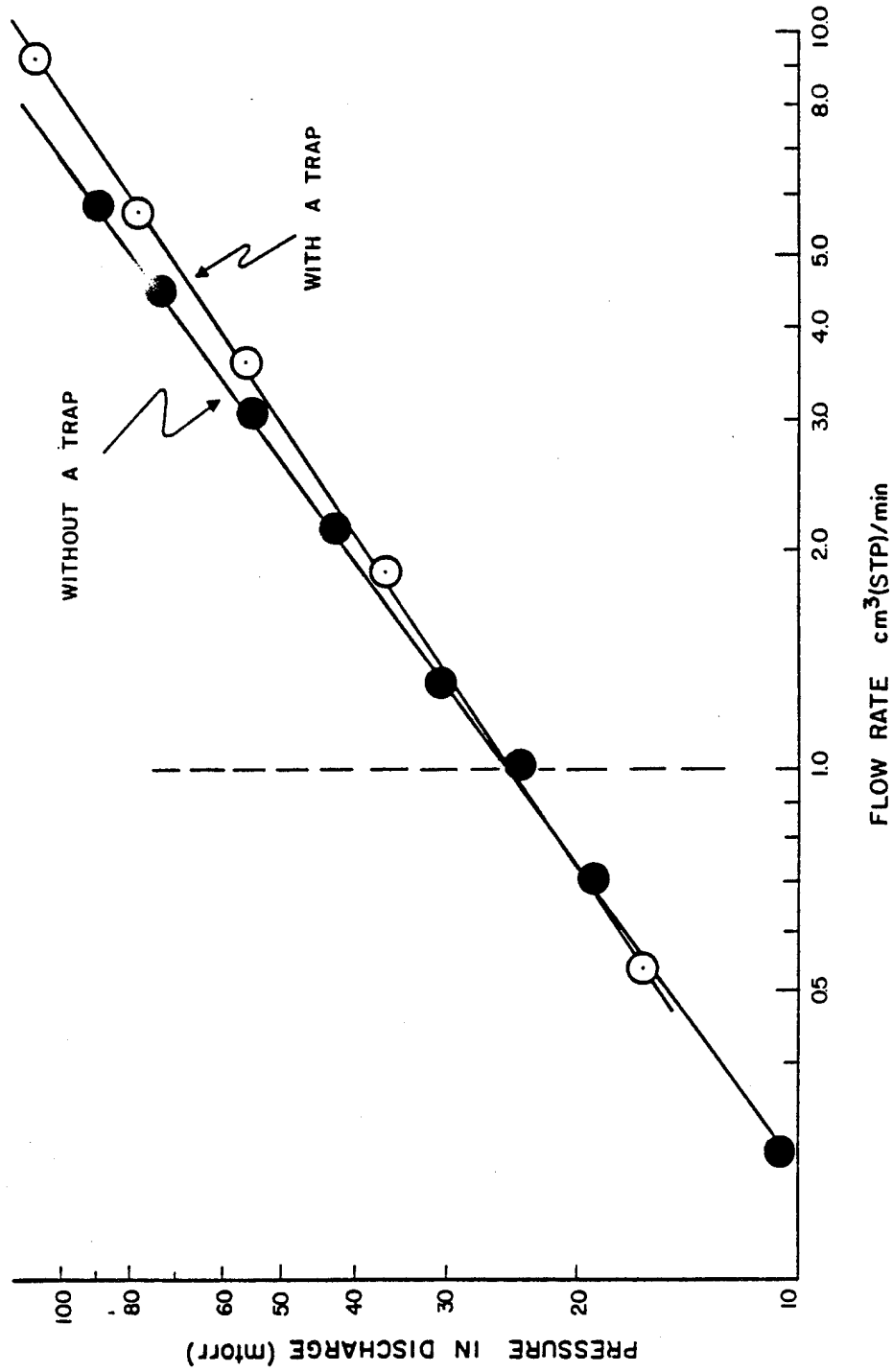
Figure 4. The dependence of system pressure during the discharge p_g on the flow rate of starting material (ethylene). Despite the difference in p_o's for systems with or without a liquid nitrogen trap, p_g is mainly dependent on the flow rate, indicating that the production rate of the product gas (H_2) and the pumping rate of a system for the product gas determine the value of p_g.

is needed to describe the discharge power for glow discharge polymerization.

In order to understand the importance of the discharge power parameter for glow discharge polymerization, it is very important to recognize the following characteristics of glow discharge polymerization: (1) the starting material is in the gas phase, but the main product is in the solid phase; (2) glow discharge polymerization occurs mainly in the glow region of a reactor; and (3) the glow region of the gas phase is not a simple plasma of the starting material but contains significant amounts of nonpolymer-forming gas product(s). Therefore, in order to describe the discharge power of glow discharge polymerization, it is necessary to express the characteristic power density in the glow volume of a flow system. Consequently, the discharge power level to describe glow discharge polymerization is a system-dependent parameter, not simply the power-input into the system.

For instance, the discharge power necessary for glow discharge polymerization (based on the maximum change which occurs in gas phase[84] of various hydrocarbons is shown in Figures 5 and 6 as a function of flow rate of the starting material. As seen in these figures, the discharge power necessary for glow discharge polymerization depends on both the molecular weight and chémical structure of the compounds.

The best first-order approach to dealing with this situation is to use the parameter given by W/FM, where W is the power input, F is the flow rate given by cm^3(STP)/min, and M is the molecular weight of starting material.[84] The parameter W/FM represents the energy input per unit mass of the starting material. The parameter W/FM does not contain terms which describe the geometric factor of and flow pattern within a reactor, and consequently the absolute value cannot be used in general cases. However, it is a useful parameter to describe glow discharge polymerization of different starting materials in a polymerization reactor.

The wide spread of discharge power shown in Figure 5 and 6 for various compounds becomes roughly comparable values when $(W/FM)_c$ is plotted against F, as shown in Figures 7 and 8. $(W/FM)_c$ represents the values of W/FM given by lines shown in Figures 5 and 6. The value $[(W/FM)_c]_{F \to 0}$ for various hydrocarbons are nearly constant, dependent
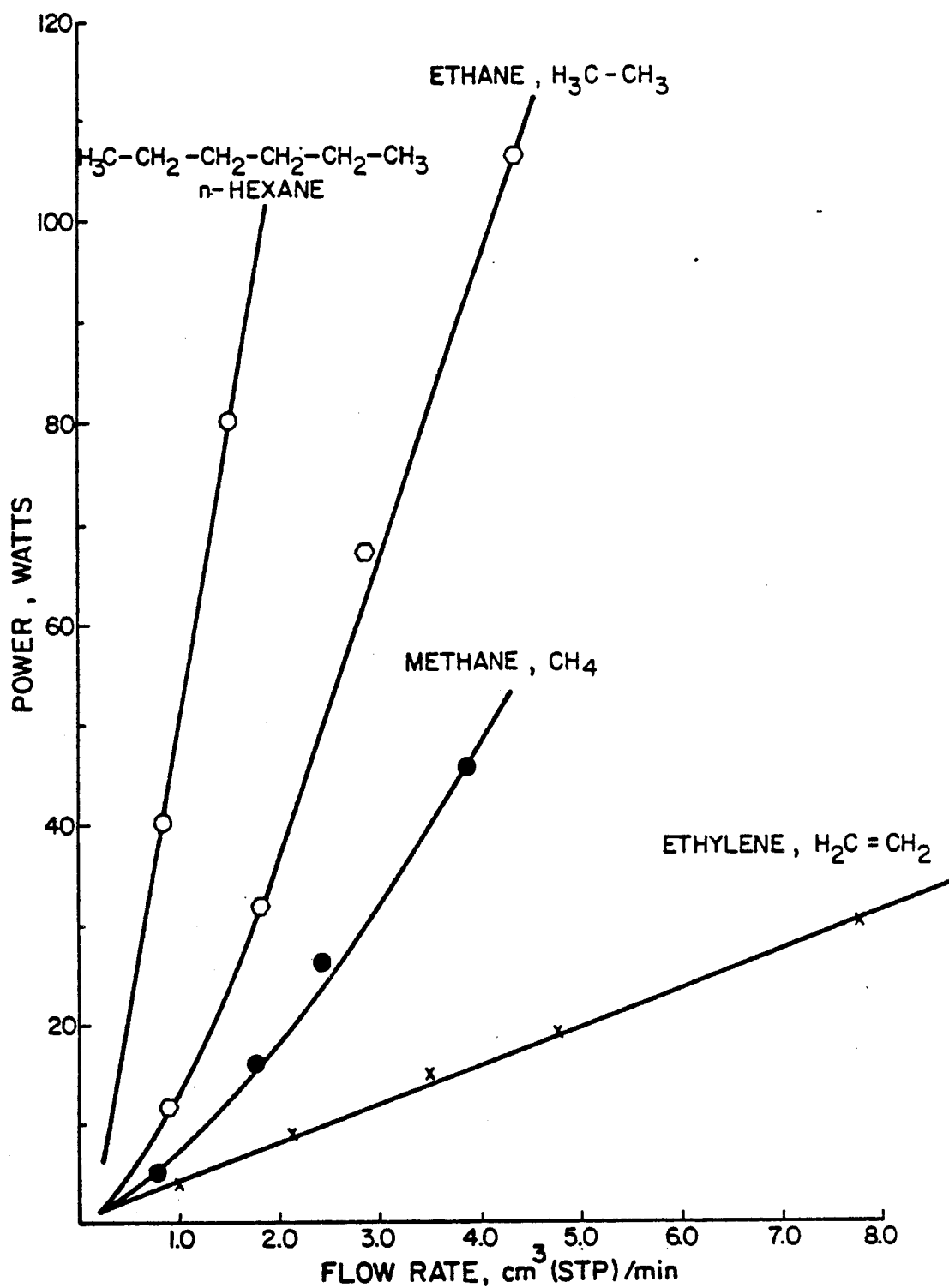
Figure 5. The dependence of discharge power to obtain a comparable level of glow discharge polymerization on the flow rates of starting materials. The discharge power is greatly dependent on the molecular weights of the starting materials.
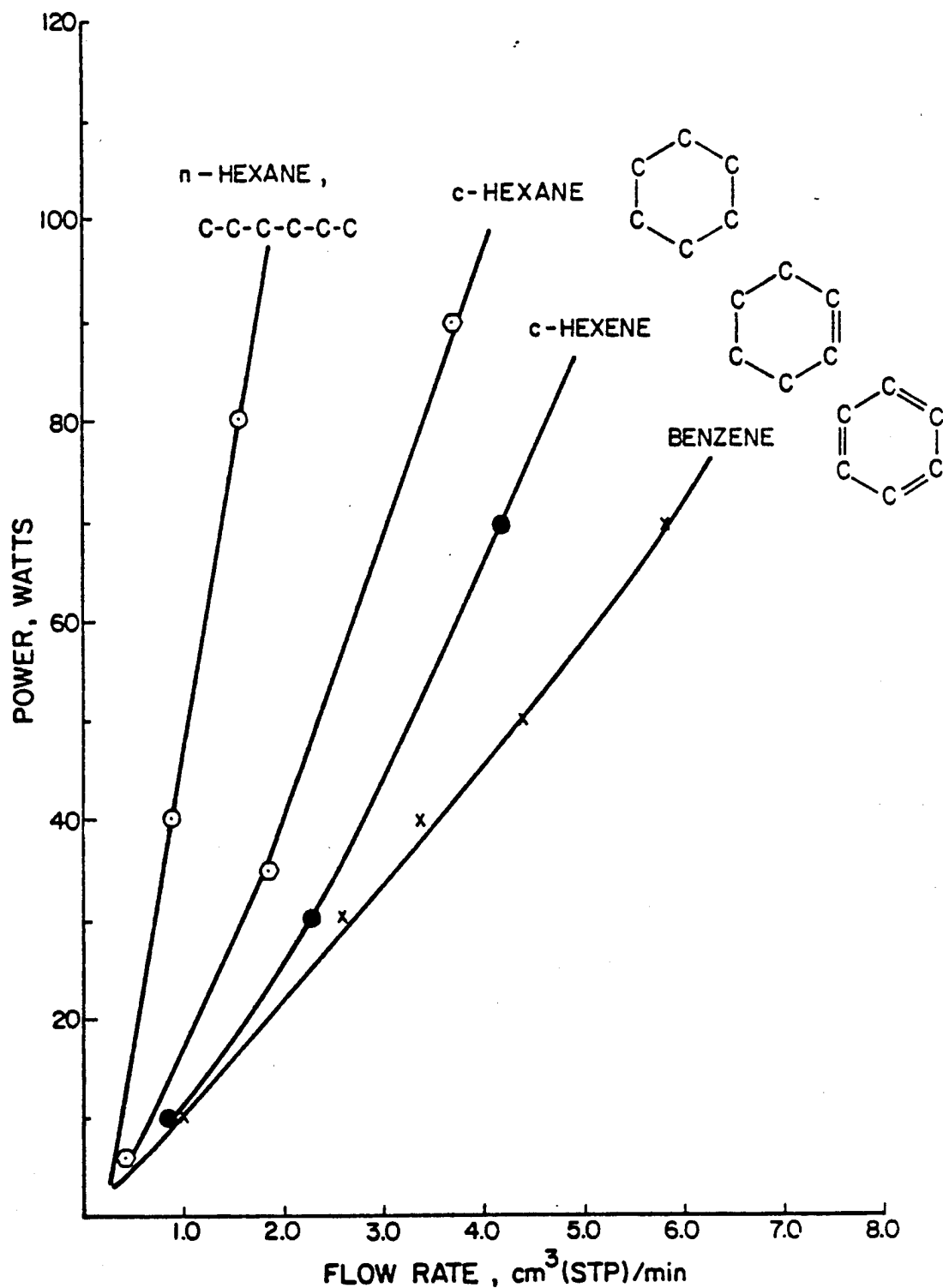
Figure 6. The dependence of discharge power to obtain a comparable level of glow discharge polymerization on the flow rates of the starting materials for hydrocarbons containing 6 carbons. The discharge power is also dependent of starting materials.
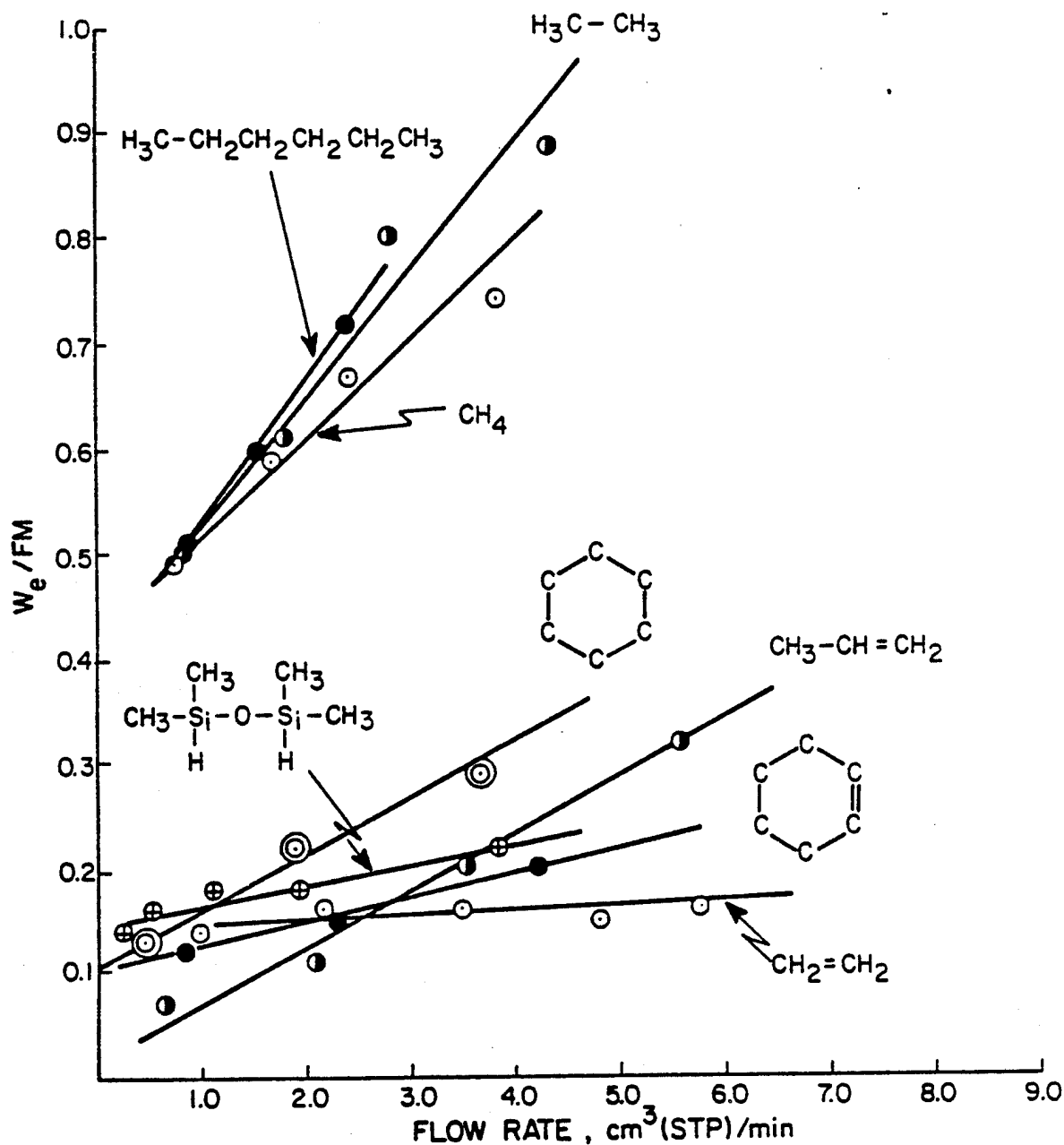
Figure 7. Plots of (W/FM)$_c$ against the flow rate for various compounds, where W is discharge power for glow discharge polymerization, F is flow rate, and M is the molecular weight of the starting material, and (W/FM)$_c$ represents the values of W/FM given by lines shown in Figures 5 and 6.
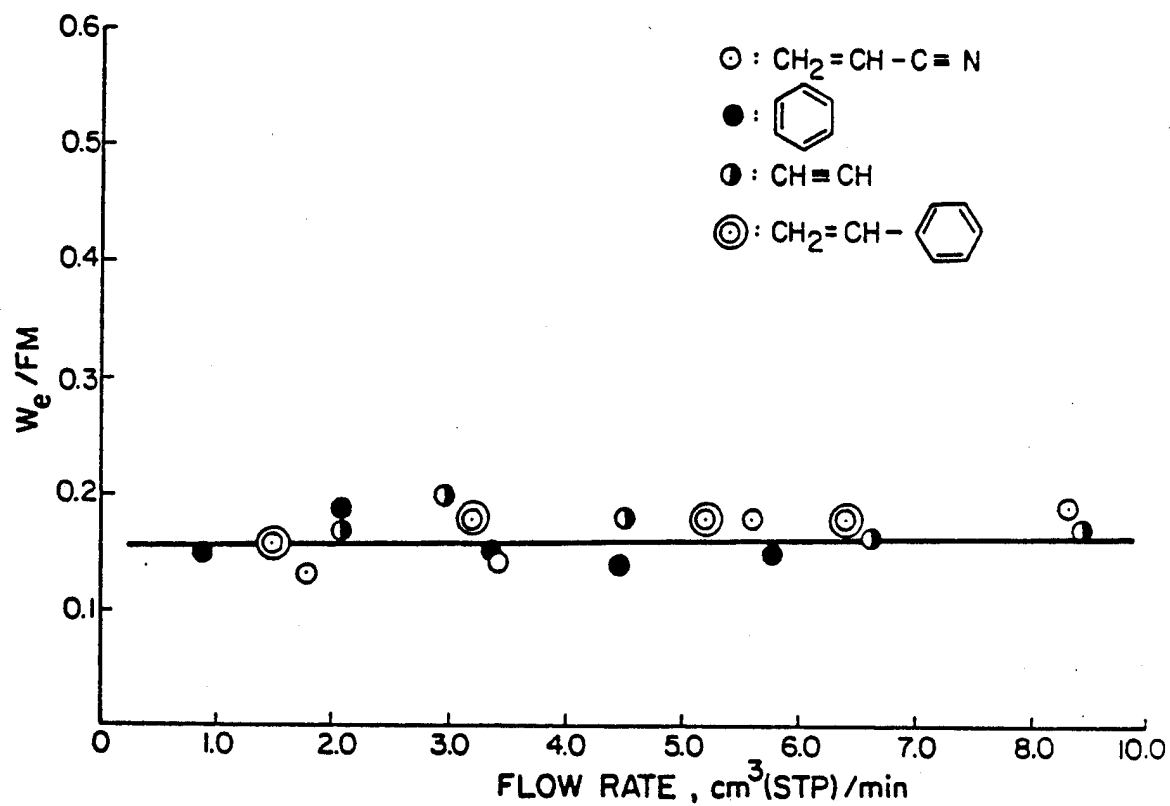
Figure 8. Plots of $(W/FM)_c$ versus the flow rate of compounds which contain triple bonds and/or aromatic structures. $(W/FM)_c$ is nearly independent of the flow rate for these compounds. (See Figure 7 for letter definitions.)

only on structures of starting materials. It is worth noting here that the slope observed in the plots of $(W/FM)_c$ vs F is proportional to the hydrogen yield of compounds, as shown in Figure 9. In order to obtain comparable glow discharge polymerization, the discharge power must be selected according to F and M.

1.2.2.5 Geometrical Factor of Reactor

1. Bypass Ratio of Flow

Not all starting materials fed into a glow discharge polymerization reactor are utilized in the polymer formation. The bypass ratio represents the portion of flow which does not contribute to glow discharge polymerization. Consequently, the higher the bypass ratio of a reactor is, the lower the conversion of the starting material is to the polymer. Clearly, this ratio depends on the ratio of the volume occupied by discharge to the total volume.

2. Relative Position of Energy-Input and Polymer Deposition

In glow discharge polymerization which utilizes internal electrodes, either the substrate is placed directly on an electrode surface or placed in the space between the electrodes.

With external electrodes or a coil, the location of the substrate can be chosen in a variety of ways. Since the polymer properties and the deposition rate are dependent on the location within a reactor, this is an extremely important factor in practical applications. The relative position is further complicated by the factor described below.

3. Relative Location of the Feed-In of the Starting Material and Flow Pattern

The location where the starting material is introduced is very important for polymer deposition. The importance of flow pattern with respect to the location of energy-input and of polymer deposition can be visualized in an example of glow discharge polymerization in a straight tube reactor with an external coil placed in the middle portion of the tube. In such a system, the volume of glow discharge is generally much larger than the volume of the portion of tube which is directly under the coil. Consequently, polymer deposition occurs even at the upstream side of the coil. The flow can best be established by avoiding all starting materials passing through the energy-input region, as seen in
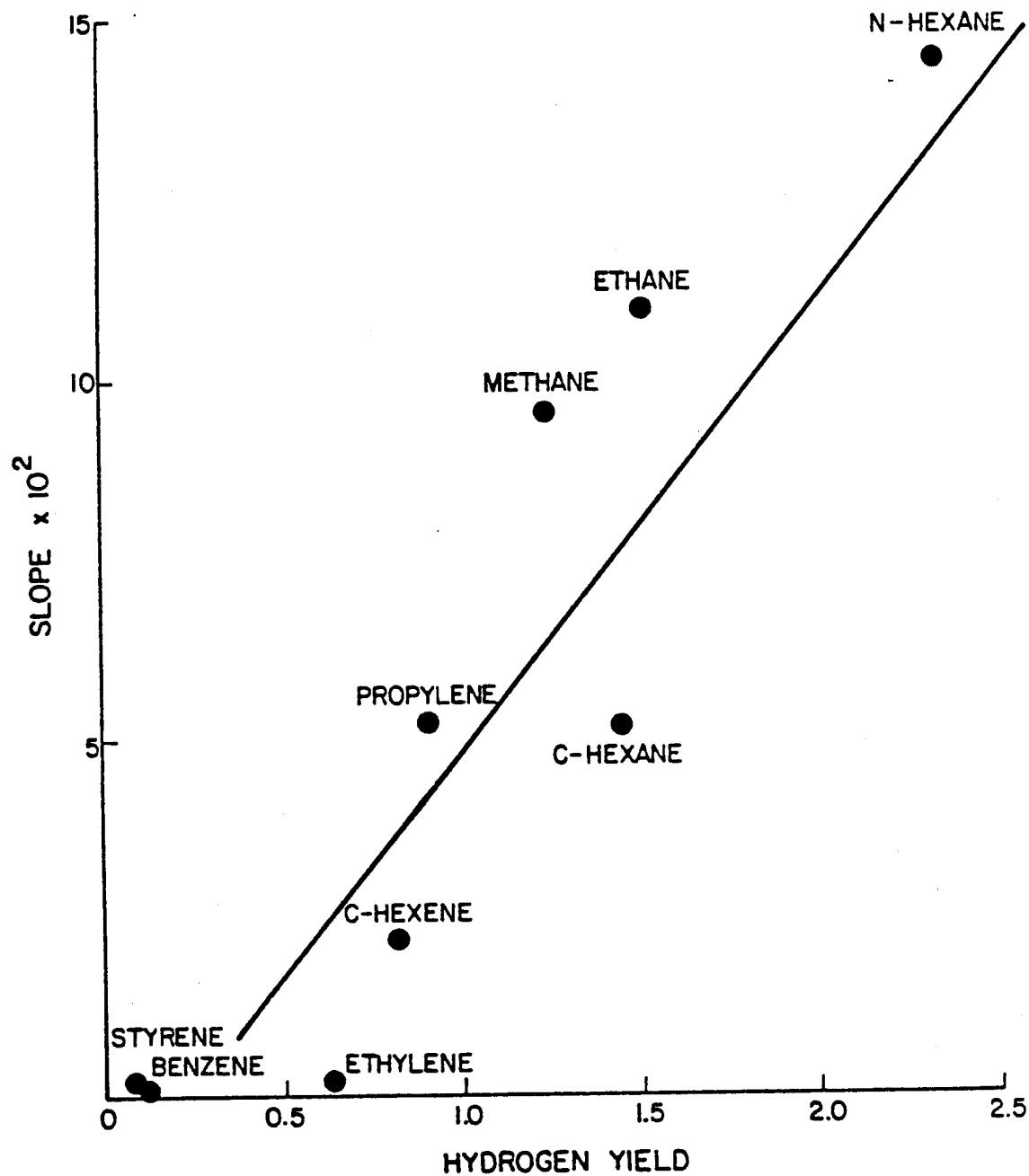
Figure 9. The dependence of the slopes of $(W/FM)_c$ vs F plots on the hydrogen yield of compounds. The hydrogen yield is the number of hydrogen molecules evolved when a molecule of starting material is incorporated into the glow discharge polymer.

the examples shown in I, II and IV of Figure 2. This factor is less obvious in a system with internal electrodes (e.g., in a bell jar).

1.2.3 Organic Compounds For Glow Discharge Polymerization

As mentioned in the introduction, nearly all organic compounds can be polymerized by glow discharge polymerization; however, the starting material should not be considered as the monomer (the starting material of polymerization in the conventional concept) of a polymerization process.

Since glow discharge polymerization can be characterized best as elemental or atomic polymerization, organic compounds can be classified based on elements contained in organic compounds.

1.2.3.1 Hydrocarbons

Hydrocarbons produce H and H_2 as the major nonpolymer-forming gas products. Since H and H_2 plasmas have little etching effect on polymers formed by glow discharge polymerization, the process of forming polymer is least affected by ablation.

Hydrocarbons can be grouped, according to their behavior in glow discharge polymerization, into the following three major groups.[85,86]

Group I.   Triple-bond-containing and aromatic compounds.

Group II.   Double-bond-containing and cyclic compounds.

Group III.   Compounds without above-mentioned structures.

Group I compounds form polymers by utilizing the opening of triple bonds or aromatic structures with the least evolution of hydrogen.

Group II compounds form polymers via both the opening of double bonds or cyclic structures and hydrogen abstraction. Production of hydrogen is considerably higher than Group I compounds.

Group III compounds polymerize primarily by plasma polymerization based on hydrogen abstraction. Consequently, hydrogen production is much higher than those for Group II compounds.

Hydrogen production per mole of starting material for typical hydrocarbons is shown in Figure 10. The discharge power necessary for glow discharge polymerization of hydrocarbons is also dependent on the types of compound. The same groupings mentioned above apply.[84] Groups I and II compounds require approximately the same energy input. However, the dependence on flow rate is nearly zero for Group I compounds, but an
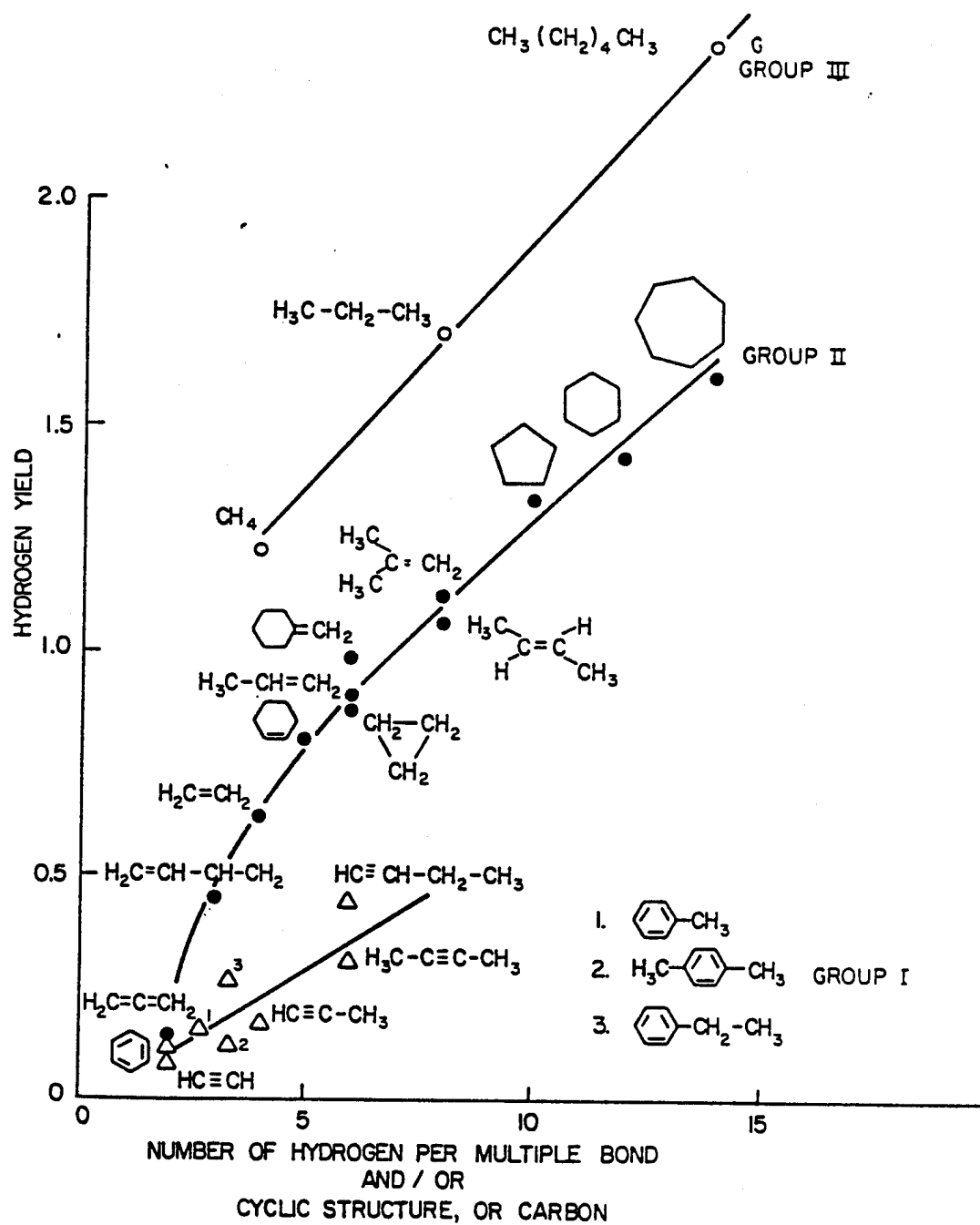
Figure 10. Number of hydrogen molecules evolved per molecule of starting material when hydrocarbons polymerize (Hydrogen Yield) as a function of chemical structure.

appreciable increase in the required energy input is observed for Group II compounds for increasing flow. Group III compounds require the highest energy input and their dependence on flow rate is much greater than that for Group II compounds (See Figures 7 and 8).

1.2.3.2 Nitrogen-Containing Compounds

Results obtained with various amines and nitriles indicate that N remains in the polymer (nitrogen does not evolve as the nonpolymer-forming product gas.[87] This tendency is in accordance with another trend[87] that N_2 gas used in a glow discharge is easily incorporated into either glow discharge polymers or polymers used as substrates.[75]

1.2.3.3 Fluorine-Containing Compounds

Glow discharge polymerization of fluorine-containing compounds, particularly of perfluoro compounds, is very sensitive to the conditions of polymerization. The use of a relatively low discharge power level is an extremely important factor for obtaining polymers from fluorine-containing compounds. High discharge power causes the detachment of F and enhances ablation. Consequently, it is often observed that no polymer is formed when glow discharge polymerization is carried out at a high discharge power, while the same compound yields polymers at a low discharge power.[88] In order to obtain a polymer by glow discharge polymerization of fluorine-containing compounds, it is advantageous to use fluorine-containing compounds which belong to Groups I and II mentioned above for hydrocarbons,[89] and/or to employ techniques that suppress the etching effect of the detached fluorine (plasma), such as the addition of a small amount of H_2[71] or hydrogen-producing compounds,[90] and use of pulsed or intermittent discharges.[89]

1.2.3.4 Oxygen-Containing Compounds

Oxygen is another of two elements (i.e., F and O) which tend to be evolved from either the starting material or substrate material, causing significant ablation of organic materials. Consequently, oxygen-containing compounds are generally poor starting materials for glow discharge polymerization. The deposition rate of polymers is generally much smaller than that of nonoxygen-containing compounds of similar molecular weight.[76] When oxygen is incorporated in chemical structures mentioned in Groups I and II for hydrocarbons (i.e., easily polymerizable structures), glow discharge polymerization proceeds with ease.[59,60] An

example of such a compound is furan where oxygen is incorporated in the ring.

1.2.3.5 Si-Containing Compounds

Si is one of the elements which has a high tendency to stay in the solid phase; therefore, glow discharge polymerization of Si-containing compounds such as silanes and siloxanes, proceed extremely well.[49,50,60] This togehter with the additional factors of relatively high molecular weight and relatively high vapor pressure of silicone-containing compounds, leads to the deposition rate obtainable from silicone-containing compounds being perhaps the highest among a variety of starting materials.[60]

1.2.3.6 Compounds Containing Other Elements

Although not enough data are available to judge behavior of compounds that contain other elements in glow discharge polymerization, a simple rule of thumb may be drawn from the CAP scheme of glow discharge polymerization. Elements which are reactive and exist in the gas phase in the normal temperature range favor the ablation process and do not contribute to polymer formation. However, it is possible that many unusual elemets which are not incorporated in conventional polymers could be incorporated into thin films formed by glow discharge polymerization.

1.2.4 Dependence of Glow Discharge Polymerization On Processing Factors

In glow discharge polymerization as a means of thin film formation, the following aspects and their dependence upon the operational or processing factors seem to be of utmost practical importance. As mentioned earlier, however, many operational factors affect glow discharge polymerization in a complexly interrelated manner and none of the factors can be singled out as being an independent variable or the most important factor of the process. It should also be kept in mind that glow discharge polymerization is system dependent, and consequently the trends or conclusion based on data obtained in a particular system may not be extended to another system.

1.2.4.1 Rate of Polymer Deposition

In the practical sense, the rate at which a polymer deposits is an extremely important aspect of the process. The rate of polymer deposition can be increased by increasing the characteristic rate of polymer formation (often called polymerization rate), or by increasing the yield of polymer formation (reducing the amount of starting material that

leaves the system without being polymerized). Unfortunately the terms "polymer deposition rate" and "polymerization rate" are often used synonymously.

1. Discharge Power

The polymer deposition rate generally increases with discharge power in more or less linear fashion in a certain range of discharge power, and reaches a plateau, as shown in Figure 11. Further increase of discharge power often decreases the polymer deposition rate.

2. Flow Rate

The polymer deposition rate increases linearly with the flow rate of a starting material under ideal conditions where the conversion ratio of starting material to polymer is high or remains at a constant level. However, the change of flow rate is often associated with changes in flow pattern (affecting the yield of polymer formation or bypass ratio of the flow) and/or the efficiency of discharge power input. Therefore, the apparent dependence of the polymer deposition rate on flow rate is often characterized by a decrease of the polymer deposition rate after passing a maximum or a narrow plateau, as shown in Figure 12.

3. W/FM Parameter

As mentioned earlier, the effect of W or F cannot be determined independently since glow discharge polymerization is dependent on the combined parameter of W/FM. As long as the W/FM value remains above a critical level $(W/FM)_c$ where energy input is sufficient for polymerization, the major effect of increasing the flow rate is to increase the feed-in rate, which increases the polymer deposition rate. However, if the W/FM level drops to a certain level as F increases at a constant W, where the discharge power is not sufficient to polymerize all starting materials coming into the reaction system, the polymerization mechanism itself changes. Consequently, the polymer depostion rate decreases despite the fact that more starting materials are supplied to the reaction system. The general situation is shown in the schematic diagrams given in Figure 13.

According to the W/FM parameter, the discharge power W must be increased as the flow rate of starting materials increases, and/or as the molecular weight of the starting material increases.
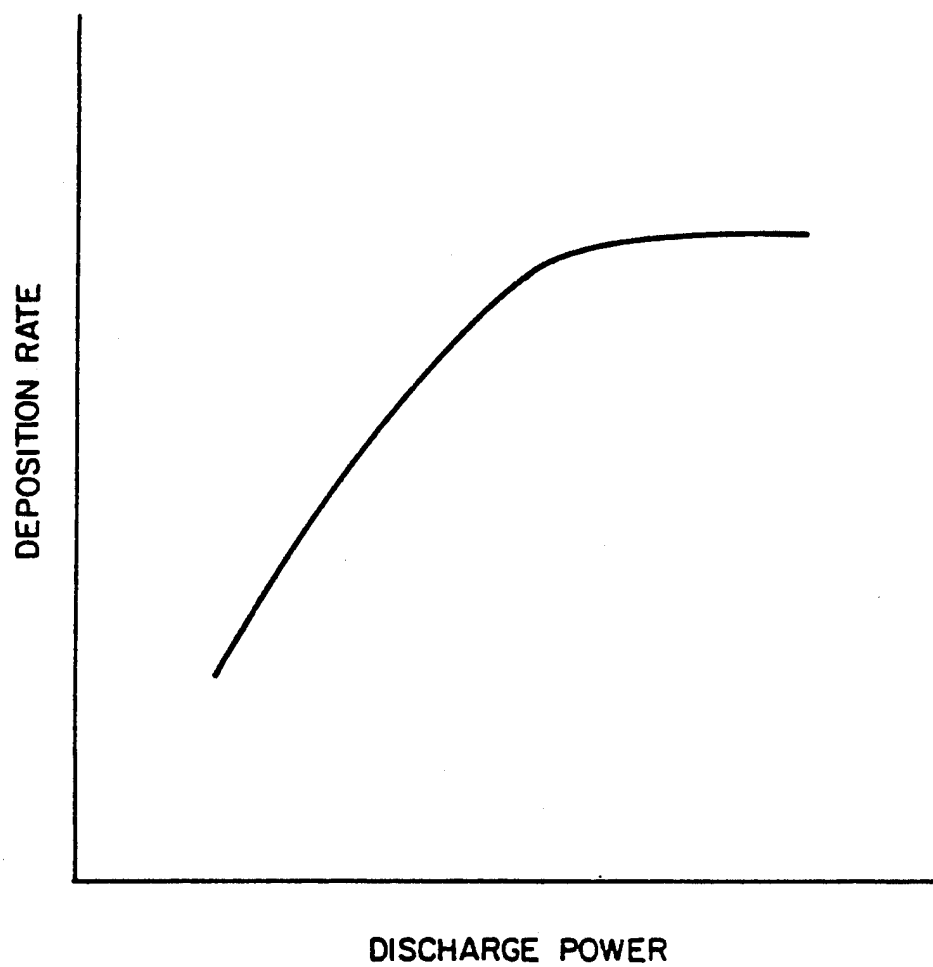
Figure 11. Schematic representation of the dependence of polymer deposition
            rate on discharge power when a constant flow rate is employed.
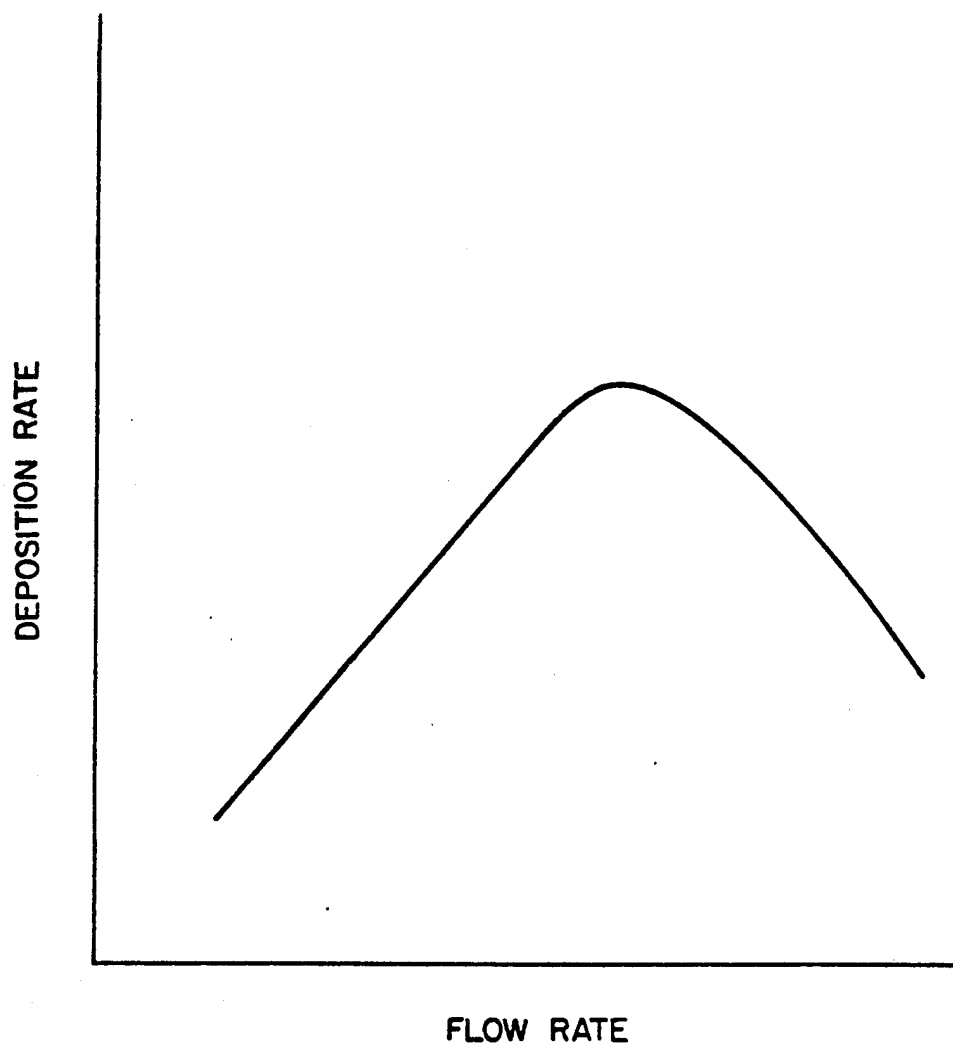
Figure 12. Schematic representation of the dependence of polymer deposition
rate on flow rate of a starting material when a constant discharge
power is employed.

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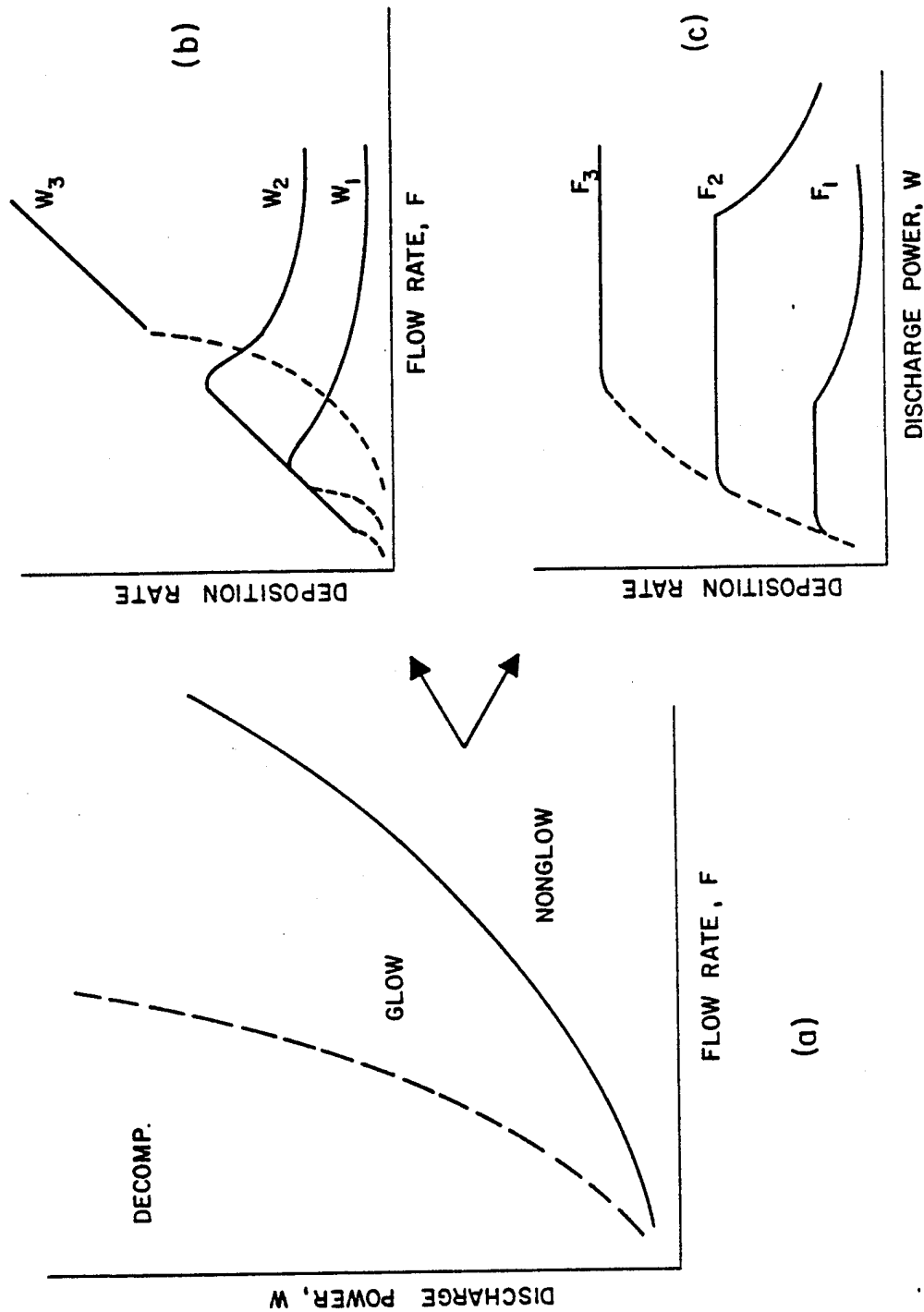
Figure 13. Schematic representation of the interrelationship of polymer deposition rate with flow rate and discharge power: a) indicates the power-flow domains of decomposition (poor polymer deposition due to predominanting ablation process), normal glow where glow discharge polymerization occurs, and nonglow region, b) and c) at a fixed level of W or F, change of F or W crosses the domain shown in (a), and consequently the apparent dependence of polymer deposition rate on either F or W is determined by where the change of domain occurs.

1.2.4.2 Distribution of Polymer Deposition

The distribution of polymer deposition is directly related to the uniformity of the thin film formed by glow discharge polymerization. Distribution of polymer deposition is dependent on (1) the geometrical arrangement of inlet of starting material, outlet of the system, and region of energy input; (2) the operating pressure of the discharge (not the initial pressure); and (3) the reactivity of a starting material to form polymers. The effects of these factors on the distribution of polymer deposition may be visualized from the data shown in Figure 14-19 obtained from an rf (inductively coupled) discharge.[91-93] The general trends are as follows.

1. The lower the discharge pressure, the wider is the distribution of polymer deposition. The lower the pressure, the larger is the mean free path of gas molecules and the diffusional displacement becomes more efficient. Therefore, the polymer formation is not localized at either the region of excitation or site of introduction of the starting material.

2. The higher the reactivity of the starting material (to form polymer), the narrower is the distribution curve of polymer deposition, which has the maximum in the vicinity of the starting material inlet.

3. With starting materials that have low reactivity, the maximum peak is shifted towards the downstream side of the inlet. Consequently, the minimum (rather than the maximum) in the distribution curve is often observed at the vicinity of the inlet.

4. Addition of nonpolymer-forming gas (e.g., Ar) tends to narrow the distribution curve.

The distribution of polymer deposition onto the surface of internal electrodes is generally very smooth, unless the starting material inlet is placed too close to the electrodes or too small an electrode gap (in relation to the mean free path of gases) is employed. The effect of inlet-outlet locations in a bell-jar-type reactor is shown in Figure 20.[94]

Regardless of the mode of electric discharge or type of reactor, the region where glow discharge polymerization occurs is located in the direct or tortuous pathway of the starting material from the inlet to the outlet. On this pathway, starting material is consumed to form a
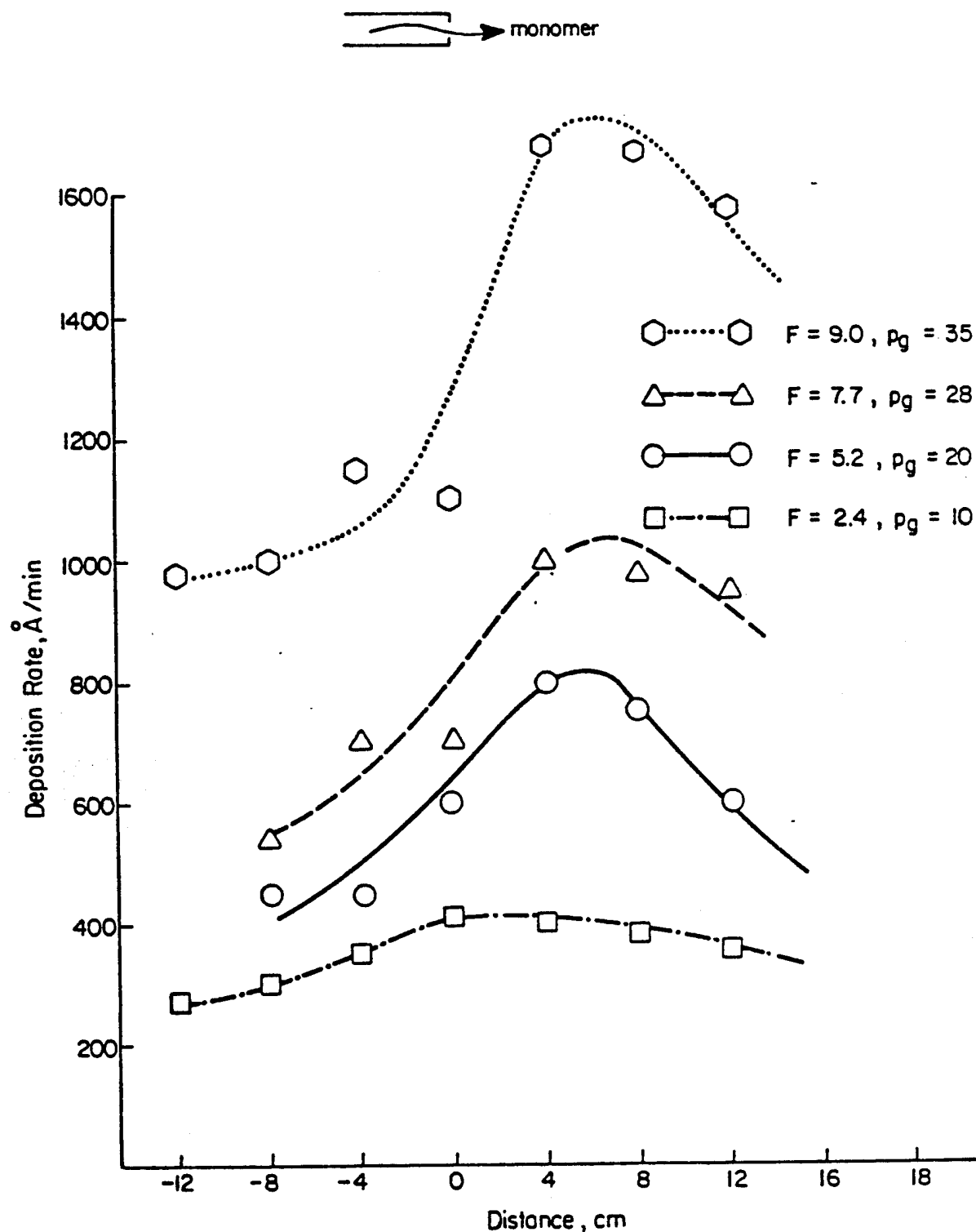
Figure 14. Distribution of polymer deposition in glow discharge polymerization of acetylene at various flow rates. F denotes flow rate in cm^3 (STP)/min, and p_g the system pressure in the glow discharge given in mtorr. The distance is taken from the point of the starting material inlet in the direction of flow. See Reference 91 for details of the reactor.
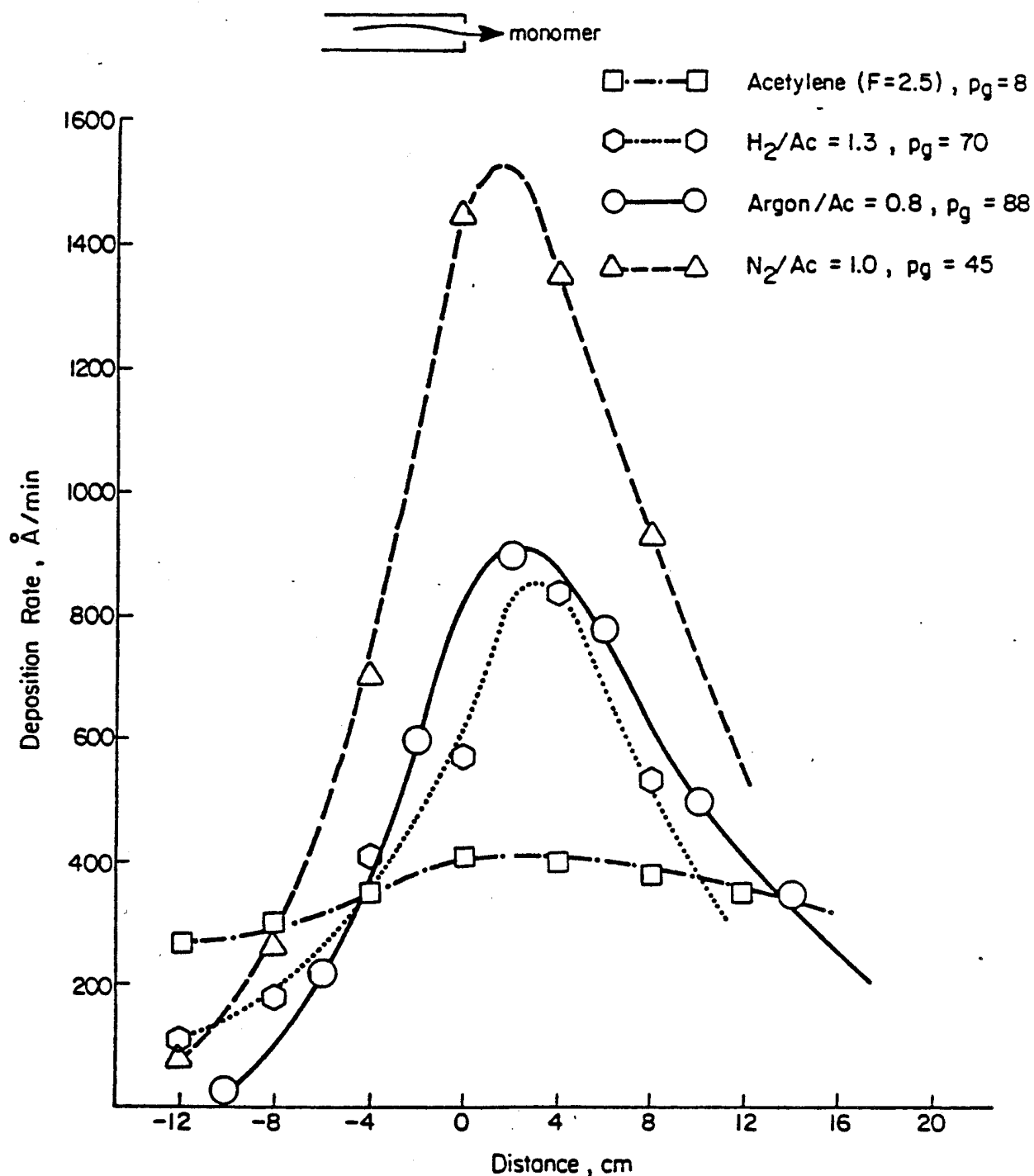
Figure 15. Distribution of polymer deposition in glow discharge polymerization
of acetylene with the addition of a carrier gas. H_2/Ac, Argon/Ac,
and N_2/Ac devote the mole ratios of carrier gas to acetylene. The
flow rate of acetylene is maintained constant in all cases. Other
notation and units are the same as those in Figure 14.
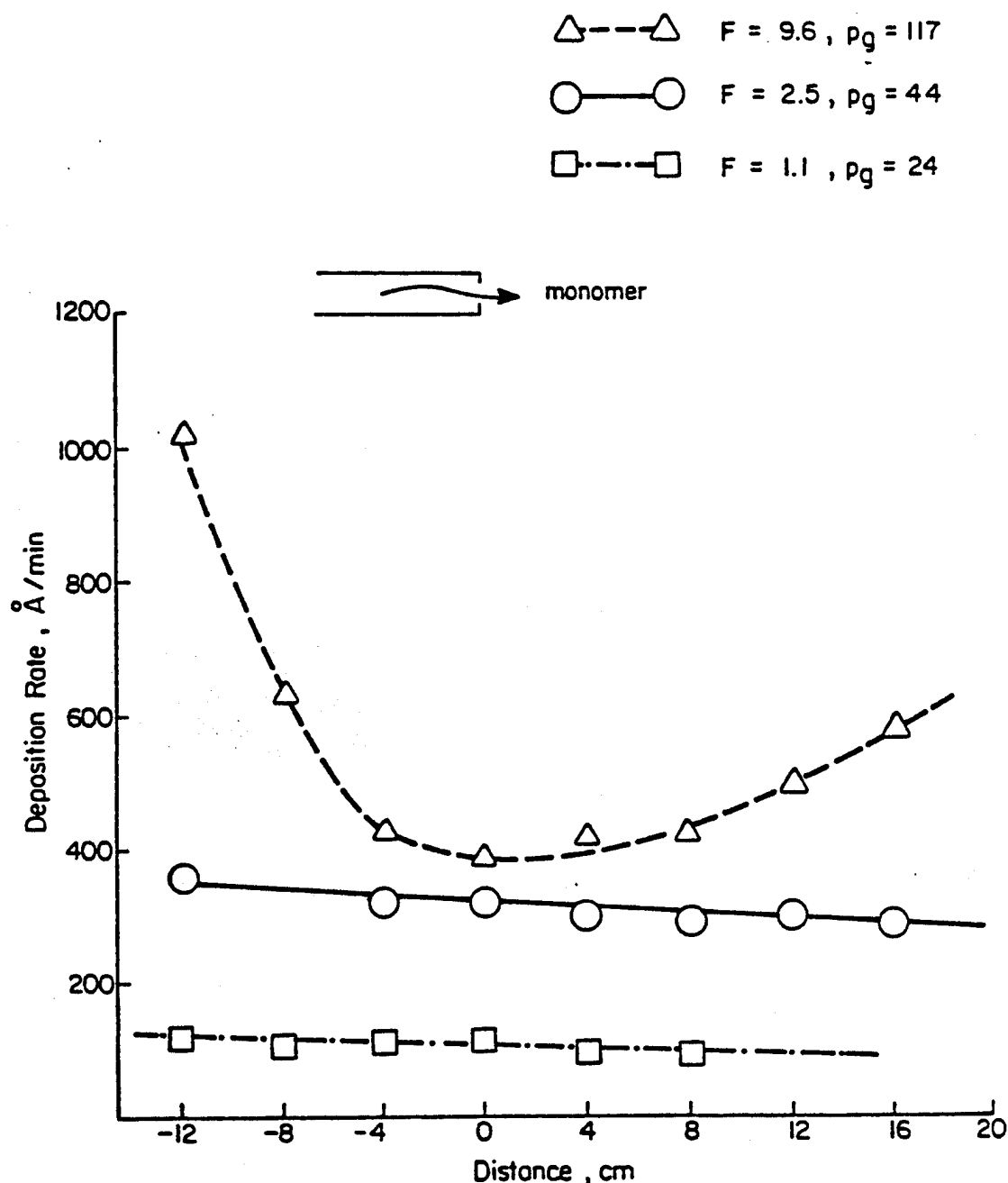
Figure 16. Distribution of polymer deposition in the glow discharge polymerization of ethylene. All notation and units are the same as those in Figure 14. Ethylene is a less reactive material than acetylene, as far as glow discharge polymerization is concerned. The increase of flow rate yields a maximum of deposition in the downstream side of the inlet, consequently the apparent minimum is observed near the inlet.
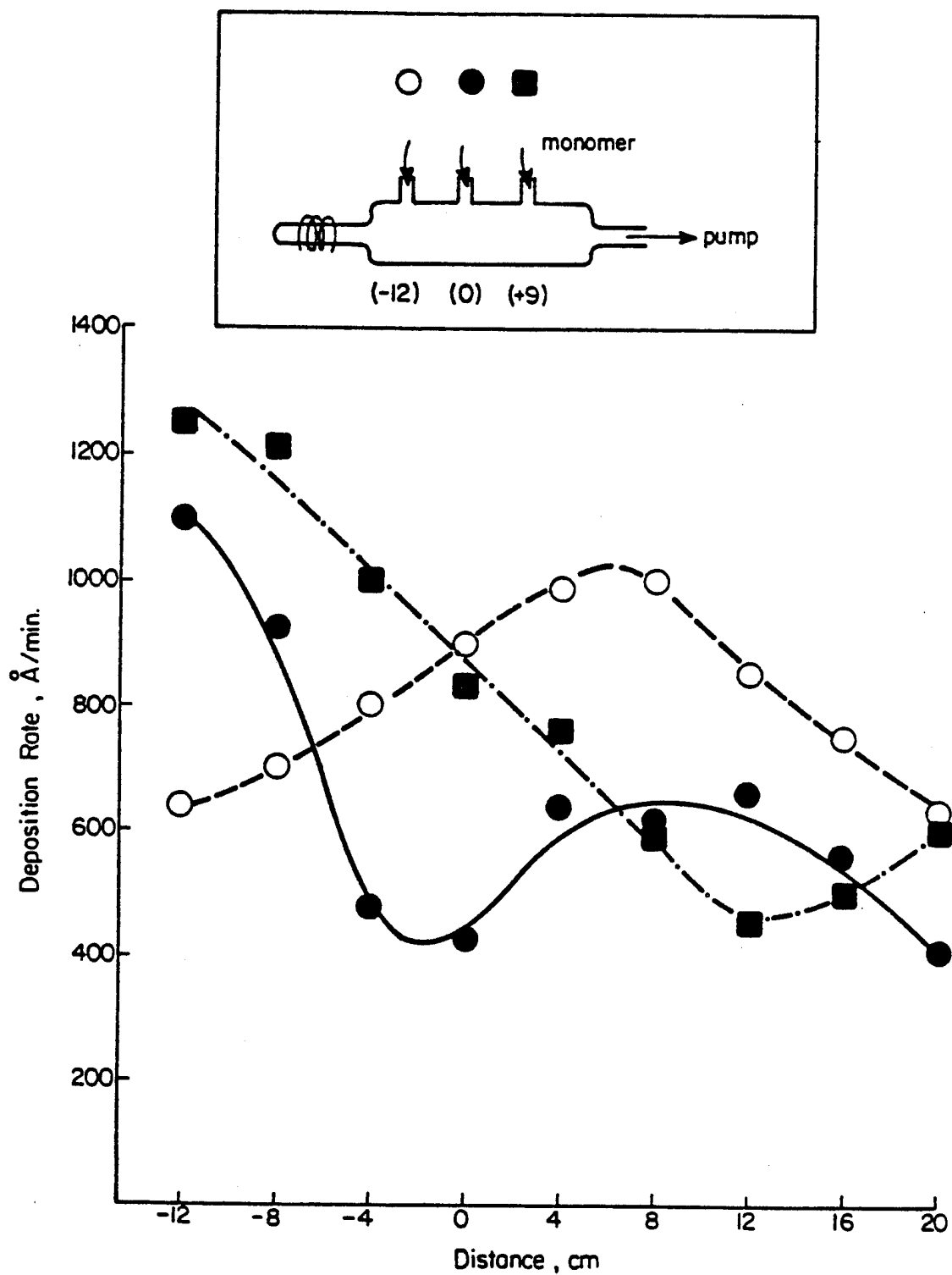
Figure 17. The effect of location of the starting material (ethylene) inlet
on the distribution of polymer deposition. The location of the
inlet is shown in the insert. The flow rate of ethylene is
maintained constant ($F = 9.8$ cm^3(STP)/min) in all cases.
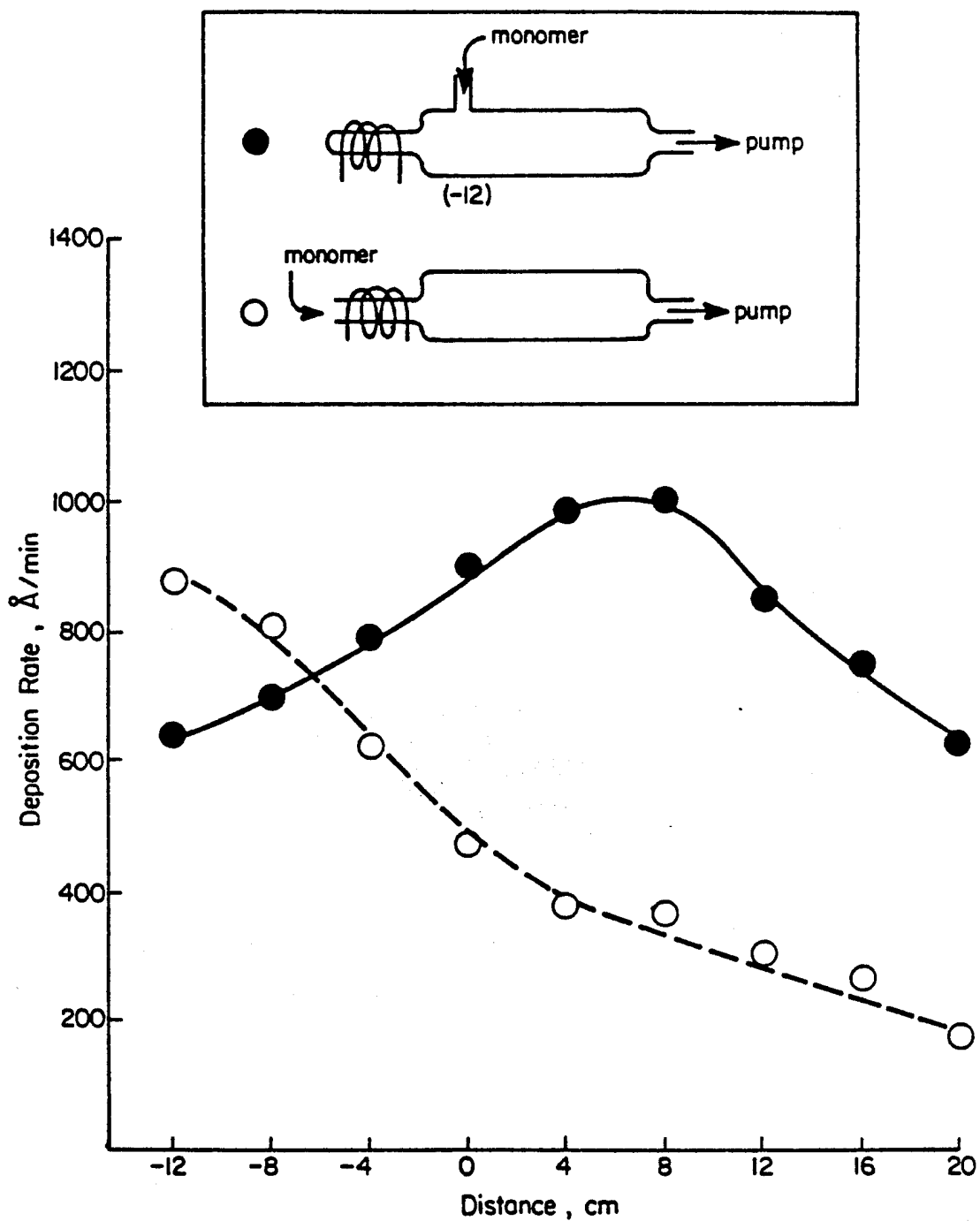
Figure 18. The effect of flow passing through the rf coil (energy input region) on the distribution of polymer deposition in glow discharge polymerization of ethylene. $F = 9.8$ cm^3(STP)/min for both cases.
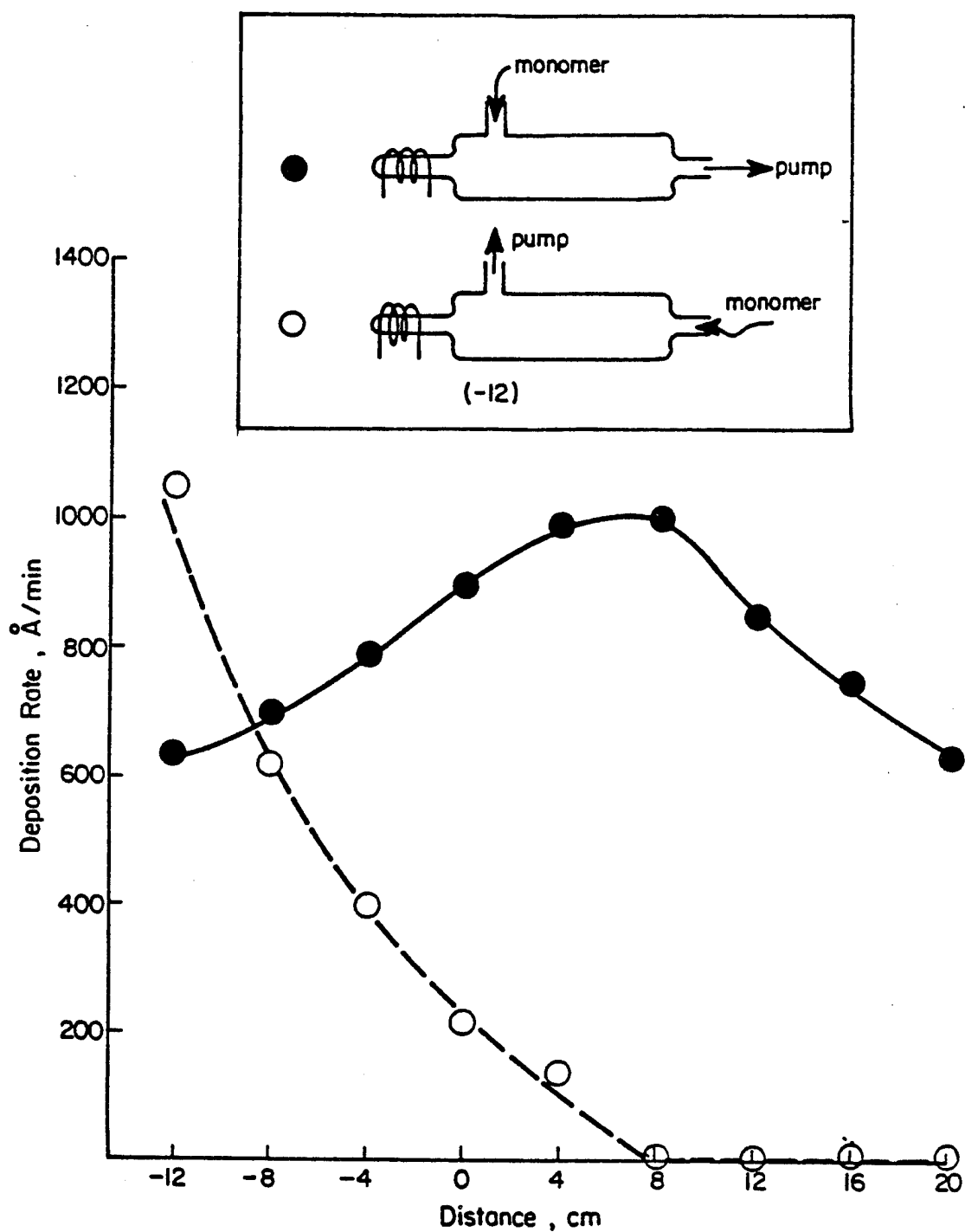
Figure 19. The effect of direction of flow in relation to the rf coil (energy input region) on the distribution of polymer deposition in glow discharge polymerization of ethylene. All other conditions are maintained constant for both cases.
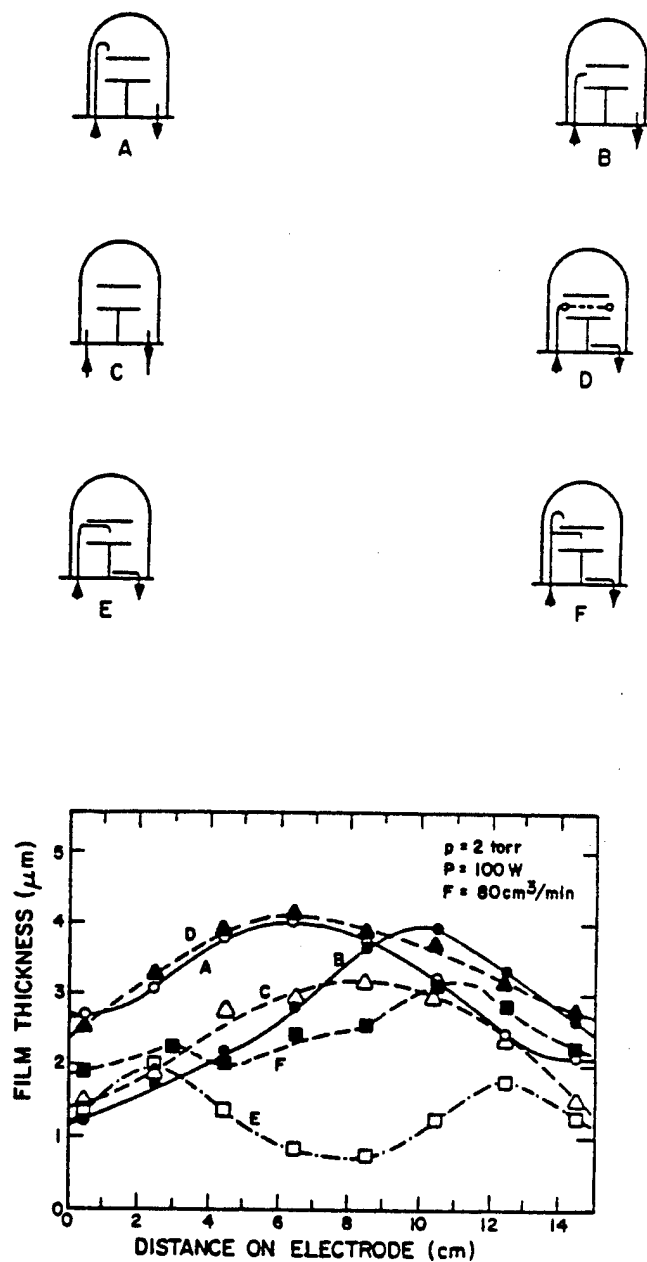
Figure 20. Effect of relative location of starting material inlet, outlet,
and electrodes on the distribution of polymer deposition onto
electrode surfaces. See reference 94 for details of conditions.

polymer, and simultaneously the gas phase changes from the starting material to the gas product as polymerization proceeds. Therefore, an uneven distribution always exists if the polymer is collected on a stationary substrate surface. A moving substrate will average out this inherent, uneven distribution of polymer deposition, and provides a practical means of yielding a uniform coating.

The distribution of polymer deposition should be taken into consideration when the polymer formation is monitored at a fixed location. The shift of the distribution curve due to changes in operational factors could be misinterpreted as a change in the polymer deposition rate itself.

1.3 Properties of Polymers Formed by Glow Discharge Polymerization

1.3.1 Dependence of Polymer Properties on Conditions of Glow Discharge

Since glow discharge polymerization is system dependent, the properties of polymers formed by glow discharge polymerization are also dependent on the conditions of the process. The properties of polymers are dependent not only on the kind of reactor used but also on the location within a reactor where polymer deposition occurs.

The diagrams presented in Figure 21[95] show what kinds of polymers are formed from a given starting material, depending upon the apparent operational factors described. Because the strict meaning of parameters, such as flow rate, pressure, etc., depends on the geometrical factors of a reactor and the type of starting material, generalization of trends should not be made from such a diagram. However, it clearly shows the important fact that the properties of polymers formed by glow discharge polymerization are entirely dependent on how the polymerization is carried out.

Analysis of polymers collected in different sections of a system, and of polymers formed by different electric discharges, also shows considerable differences in their properties.[96,97]

A study of the properties of polymers formed from tetrafluoroethylene by glow discharge polymerization investigated by Electron Spectroscopy for Chemical Analysis (ESCA)[98] provides further evidence of the importance of processing factors. Tetrafluoroethylene is an ideal starting material
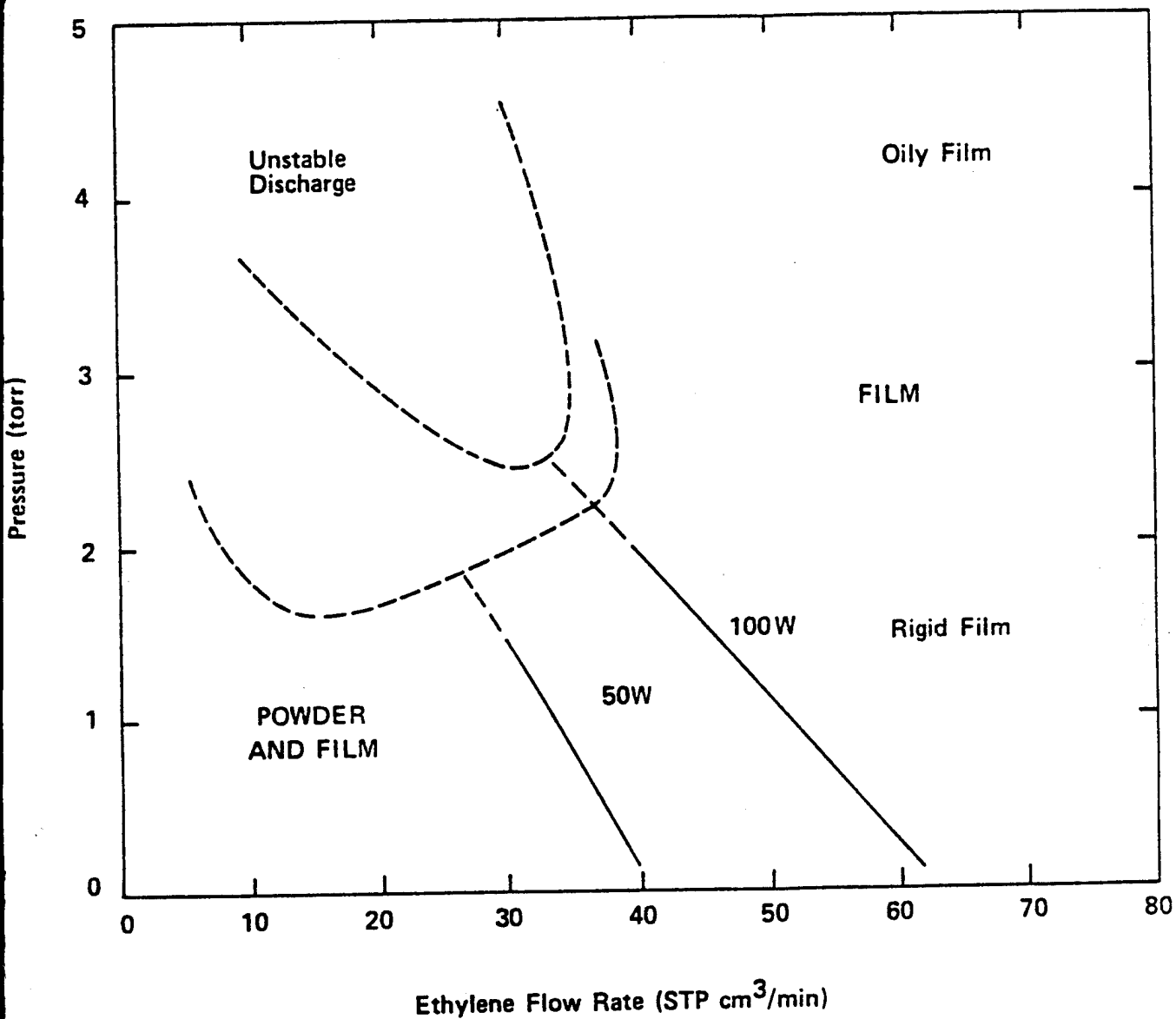
Figure 21. An example of the dependence of the type of polymer formed on the apparent operational factors of power, pressure, and flow rate.

to illustrate the CAP scheme of glow discharge polymerization. Therefore, some results are shown in Figures 22-24.

The ESCA Cls spectrum of conventionally prepared polytetrafluoro-ethylene shows a single intense peak at 292 eV corresponding to the -CF_2- carbon bond. The peaks at binding energy levels of less than 291 eV represent the presence of cross-links (>CF-, <Cf<) and carbons bonded to other substituents, including nitrogen- and oxygen-containing groups.

Characteristic shapes of the Cls peaks shown in Figure 22 indicate that polymers that are fomed at locations in the upstream side and in the downstream side of the rf coil are quite different when a relatively low discharge power is used. The polymer formed in the upstream side contains considerable amounts of CF_3 and CF besides the expected CF_2. This is undoubtedly due to the elemental or atomic nature of glow discharge polymerization rather than conventional molecular polymerization.

The polymer formed in the downstream side of the rf coil at this low discharge power contains much less F (i.e., much smaller peaks for higher binding energy) and the peak at 284.6 eV becomes the major peak. This is a dramatic display of the effect of the energy input zone (i.e., tube directly under rf coil) on the properties of glow discharge polymers. As the discharge power is increased, this severe effect of the energy input zone expands eventually to the entire length of the tube and at a high discharge power, the polymer formed in the upstream side of the rf coil becomes similar to the polymer formed in the downstream side, as seen in Figure 23.

When a system in which the flow does not pass through the energy input zone and glow discharge polymerization is carried out in the tail-flame portion of the glow discharge, the polymer formed at the downstream end of a reactor is not necessarily the same as that formed in the downstream end of a straight tube. Results given in Figure 24 show that the polymer formed in the nonglow region, although it is located at the downstream end of a reactor, is nearly identical to the conventional polytetrafluoroethylene. This means that polymers formed under such conditions are formed mainly by plasma-induced polymerization.

As mentioned earlier, tetrafluoroethylene is a special starting material which reflects the effects of operational factors in a very
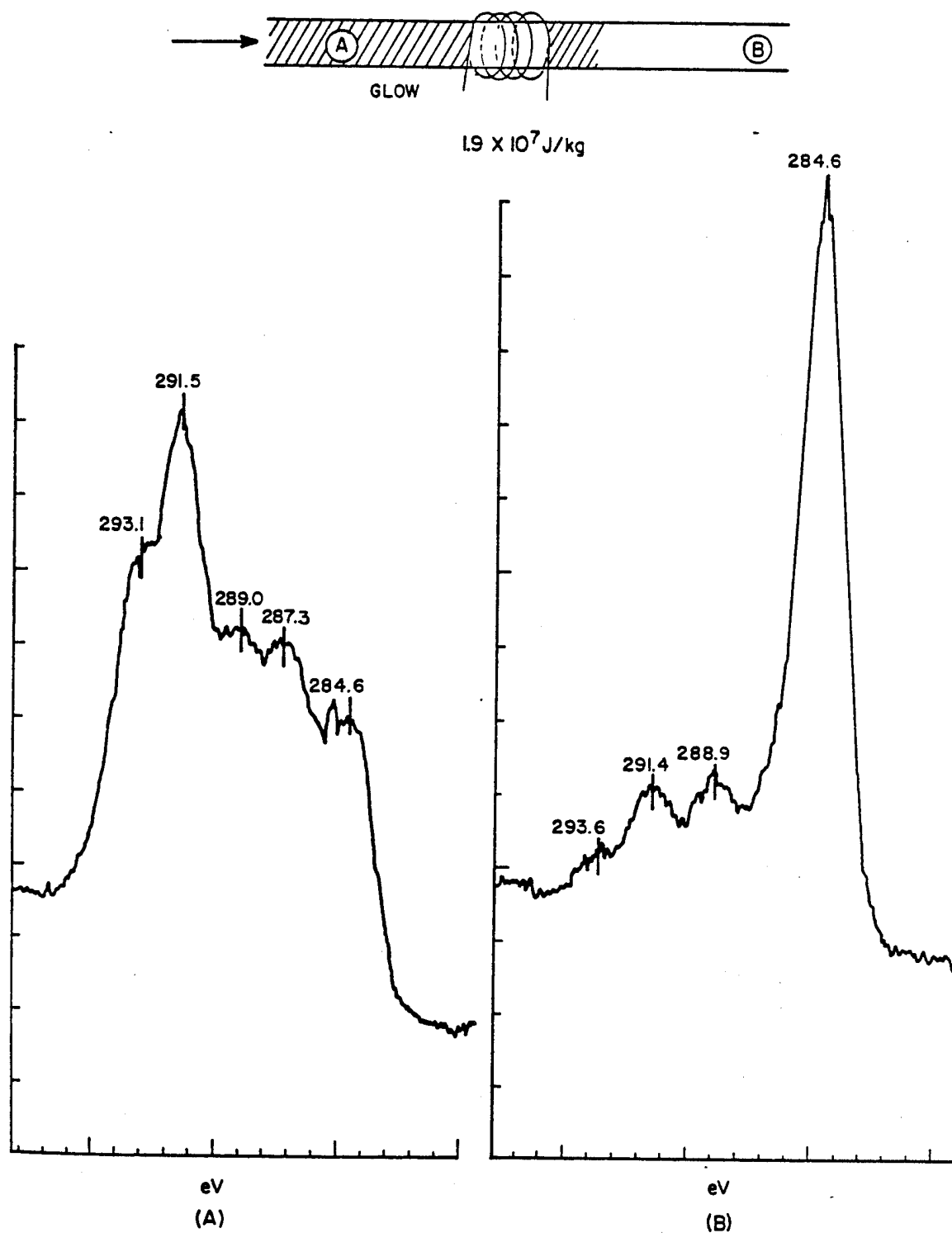
Figure 22. Dependence of the ESCA C1s peaks of glow discharge polymers of tetrafluoroethylene on discharge conditions and the location of polymer deposition. Polymer deposit occurred at two locations (a) before the rf coil, and (b) after rf coil. Discharge power level is 1.9 x 10^7 Joules/kg.

Figure 23. ESCA Cls peaks of glow discharge polymers of tetrafluoroethylene
            in the same reactor shown in Figure 22, but at the higher dis-
            charge power level of 7.7 x 10^8 Joules/kg.

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Figure 24. ESCA Cls peaks of glow discharge polymers of tetrafluoroethylene prepared in a reactor shown in the insert: (c) at the end of the glow region, and (d) at the end of the tube in the nonglow region.

sensitive manner. Therefore, some effects (e.g., the increase of abla-
tion by the increase of discharge power and by the location within a
reactor) might be much smaller with other starting materials. However,
the important aspects of (1) elemental or atomic polymerization and (2)
system dependent polymerization, would be undoubtedly applicable to many
other starting materials. These effects should be taken into consider-
ation in designing the reactor, during processing, and in interpretation
of results.

1.3.2 Characteristics of Glow Discharge Polymerization

In order to understand the characteristic feature of glow discharge
polymers and in particular, with respect to the conventional polymers,
it seems necessary to compare the mechanisms or principles of polymer
formation in glow discharge polymerization and in the conventional
(molecular) polymerization. Some important aspects which are essential
in proper understanding of glow discharge polymerization are discussed
in the following sections.

1.3.2.1 Molecular Polymerization Vs. Atomic Polymerization

Atomic polymerization is the principal element of the CAP mechanism
but a similar result may be expected if one conceives of a polymerizable
precursor. The formation of polymers from organic compounds, which do
not polymerize under normal conditions, may be postulated by assuming
that polymerizable precursors are formed in the plasma-state and form
polymers by conventional polymerization mechanisms. For instance, the
slower polymer deposition from ethylene compared to that from acetylene
has been attributed to the slower process of forming acetylene, which is
assumed to be the precursor of glow discharge polymerization.[99] According
to this concept, saturated hydrocarbons, such as methane and ethane,
will polymerize via plasma synthesis of acetylene and subsequent (mole-
cular) polymerization. The frequently disputed subject of vapor phase
polymerization versus surface polymerization is discussed in the context
of precursor concept (although it is usually not mentioned explicitly)
because one cannot explain the polymerization of saturated hydrocarbon,
such as CH_4, without assuming such a precursor.

There is no clear-cut answer to whether atomic polymerization
theory or precursor theory better explains the actual process of polymer

formation in glow discharge because there is no direct evidence to prove
or disprove either. All experimental data in glow discharge polymeriza-
tion can be interpreted only as circumstantial evidence so far as the
mechanism of polymer formation is concerned. Therefore, the following
discussion, presented to support the concept of atomic polymerization,
is not intended to disprove any other concept but is intended to present
a new way of recognizing glow discharge polymerization. The most impor-
tant point is that any theory must cover all possible cases and must
satisfactorily explain not only one aspect of glow discharge polymeriza-
tion, e.g., polymer deposition rate, but all other aspects, e.g., dis-
tribution of polymer deposition and change of polymer properties associ-
ated with the distribution, in a consistent manner.

The following arguments used to support the concept of atomic
polymerization are not necessarily consistent with others presented in
the literature. This can be attributed to the fact that glow discharge
polymerization is highly system-dependent, and the definition and expres-
sion of experimental conditions have been rather ambiguous. For instance,
glow discharge polymerization has been customarily carried out under
arbitrarily chosen experimental conditions, such as with a fixed discharge
wattage and at a fixed flow rate, but a satisfactory comparison of the
glow discharge polymerization of two different monomers cannot be made
in such a manner. Because the minimum discharge wattage necessary to
effect the glow discharge polymerization of a given monomer, e.g.,
ethylene, can differ greatly from that for another, e.g., n-hexane, it
becomes immediately obvious that a comparison of these two monomers
cannot be made at a fixed discharge wattage. The data used in the
following discussion are based on the conditions of glow discharge
polymerization described in detail by Yasuda and Hirotsu.[100]

1.3.2.2 Correlation Between Polymer Deposition Rate and Chemical Structure of Monomer

When polymer deposition rates are compared for various pairs of
monomers, which have similar chemical structures with and without vinyl
double bonds, the difference between those with olefinic vinyl double
bonds and those without is very small[85] as shown in Table II. Further-
more, the differences among various kinds of monomers are surprisingly

Table II. Comparison of Polymer Deposition Rates[a] for Vinyl and Saturated Vinyl Compounds.

Vinyl monomer		Saturated vinyl monomer	
Compound	$k \times 10^4$ (cm^{-2})	Compound	$k \times 10^4$ (cm^{-2})
4-Vinylpyridine	7.59	4-Ethylpyridine	4.72
α-Methylstyrene	5.33	Cumene	4.05
Styrene	5.65	Ethylbenzene	4.52
N-Vinylpyrrolidone	7.75	N-Ethylpyrrolidone	3.76
Acrylonitrile	5.71	Propionitrile	4.49
Vinylidene chloride	5.47	1,1'-Dichloroethane	2.98
Allylamine	2.86	n-Butylamine	2.52
Methyl acrylate	0.99	Methyl propionate	0.57

[a]Polymer deposition rate R in $g/cm^2 \cdot min$ is given by $R = kF_w$; F_w is the weight basis flow rate (g/min).

small. In other words, nearly all hydrocarbon monomers polymerize at rates that vary only within an order of magnitude. These two aspects indicate that no specific structure (necessary for the precursor theory) is needed for the glow discharge polymerization of organic compounds.

The dependence of polymer deposition rates on the molecular weight of monomers is another important aspect. For instance, if one takes a homologous series of saturated hydrocarbons, the probability of their forming precursor structures, e.g., acetylene, decreases rapidly as the number of carbons increases, whereas the number of hydrogen molecules evolved during glow discharge polymerization increases monotonously with the number of carbons[86] as shown in Figure 10. This indicates that every hydrogen atom has an equal probability for hydrogen abstraction. Therefore, if a precursor is formed first, the polymer deposition rate should decrease with an increase in the number of carbons in a hydrocarbon molecule. Contrary to this expectation, the polymer deposition rate increases with the molecular weight of the monomer[76] as shown in Figure 25. These correlations are in accordance with the atomic polymerization mechanism.

Characteristics of atomic polymerization are directly seen in the incorporation of gases or vapors, such as N_2, CO, and H_2O, by polymers formed in glow discharge, when these gases or vapors are mixed with the vapor of an organic compound.[77]

If the basic step of forming a polymer is molecular polymerization of the precursor species created in a plasma, the incorporation of such gases or vapors cannot be explained. This gas incorporation in glow discharge polymerization is also an indication of the atomic nature of the polymer formation process, i.e., gases and vapors provide atoms but are not incorated as molecules.

1.3.2.3 Trapped Free-Radicals In Polymers

One of the most significant features of glow discharge polymerization is that large amounts of free-radicals are trapped in the polymer.[101,102] Although the amounts of trapped free-radicals vary with the types of monomers and conditions of glow discharge polymerization, it is safe to consider that glow discharge polymers contain trapped free radicals. An explanation of how these free radicals are formed could provide important
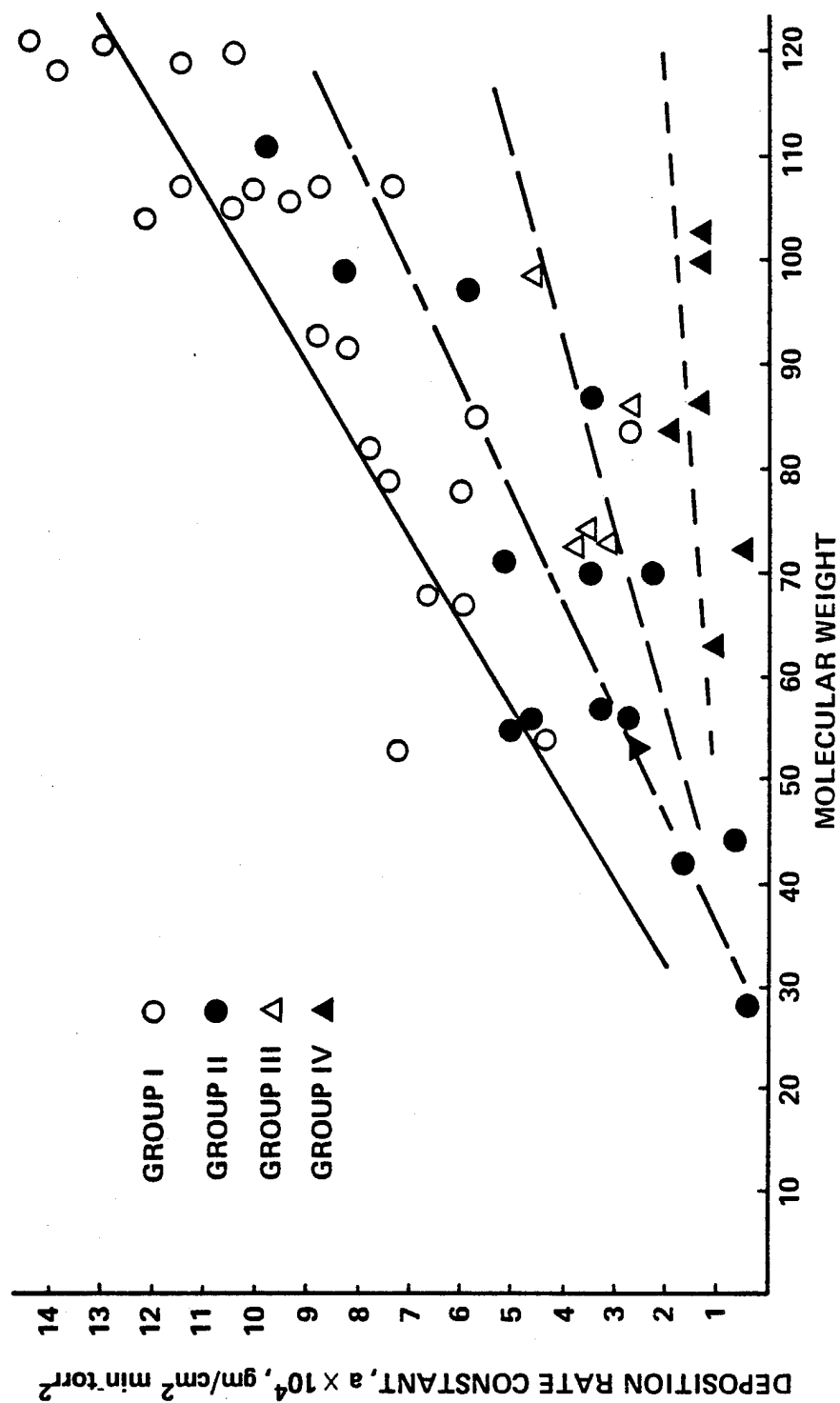
Figure 25. Dependence of polymer deposition rate on molecular weight of monomer. Group I – Triple-bond-containing, aromatic, and hetearomatic compounds. Group II – Double-bond-containing and cyclic compounds. Group III – Compounds without above mentioned structures. Group IV – Oxygen-containing compounds.

information for how polymeric materials are formed in the glow discharge of organic compounds.

Obviously, molecular polymerization, e.g., free radical polymerization of vinyl monomers, does not yield polymers with trapped free-radicals. Therefore, if one considers molecular polymerization of precursors as the main polymer forming mechanism, it is necessary to take into account separate mechanisms for creating free radicals in polymers. An easily conceived mechanism is free radical formation by radiation, because glow discharge can be considered as a kind of radiation process. There are many energetic species, such as electrons, ions, excited molecules, free radicals and photons, in glow discharge, consequently such a hypothesis is not at all unreasonable. Therefore, the trapping of free radicals in a glow discharge polymer as a function of the chemical structure of monomers should be examined.

First, there is a definite correlation between the spin concentration measured by ESR and the chemical structure of monomers. Glow discharge polymers of monomers that contain triple bond, aromatic, and hetearomatic rings and $-C\equiv N$ produce the highest level of free spins. Hydrocarbons can be grouped into three major types based upon their behavior in glow discharge polymerization. These can be tentatively referred to as Group I, II, and III monomers. Group I monomers are those mentioned above. They polymerize with evolution of the least amount of hydrogen and contain the highest level of free spins among polymers. Group II monomers are compounds containing an olefinic double bond and/or a cyclic structure. Group III monomers are saturated compounds, which do not contain the structures mentioned in Groups I and II. Group III monomers polymerize with evolution of the highest level of hydrogen and contain the least amount of free spins. Group II monomers lie in between these two extremes, i.e., they evolve a moderate amount of hydrogen and exhibit an inter-mediate level of free spin concentration.

Because the energy level of the electrons and ions are much lower compared to those involved in other radiation processes, such as in γ-rays and high energy electron beams, it is thought that these energetic species have no penetrating power. This agrees with the ESR data obtained with glow discharge polymers applied to glass substrates.[101] The free

spin concentration of the samples can be further divided into the free spin concentration in the glow discharge polymers and in the substrate glass tubes.

The free-spin concentration in the glass can be attributed to ultraviolet irradiation in the glow discharge polymerization system. If trapped free-radicals are formed by the irradiation of the formed polymer by molecular polymerization of the plasma synthesized precursor and, consequently, imparting no free-radicals in the polymer, the level of ultraviolet irradiation manifested by the free- spin concentration in the glass should be proportional to the free-spin concentration in glow discharge polymer. In other words, the highest free spins in glass should be obtained by the glow discharge polymerization of Group I monomers. Contrary to this expectation, the highest level of ultraviolet emission is associated with Group III monomers, which yield the least amount of free spins in the polymer as shown in Table III. This trend is in accord with the intensity of the glow observed in the glow discharge polymerization of monomers. Specifically, the glow observed for Group I is very weak, whereas the one observed for Group III is the most intense. In other words, the level of ultraviolet emission is proportional to the evolution of hydrogen in the glow discharge polymerization system. Consequently, the hypothesis that trapped free radicals are formed by irradiating polymers does not explain the forming of trapped free-radicals in glow discharge polymers. Thus, the precursor theory cannot explain the presence of large amounts of free-radicals in glow discharge polymers. That means that a radically new approach is needed to explain the formation of polymers in glow discharge.

1.3.2.4 Sputter-Coating Vs. Glow Discharge Polymerization

The atomic polymerization so far discussed can be characterized by the fact that a monomer used in glow discharge polymerization provides a source of elements but does not act as a monomer in a molecular sense. Similar phenomena can be seen in the sputtering of metals. Therefore, it may be worth comparing the sputtering process with the glow discharge polymerization of organic compounds.

The sputtering of metal is usually conducted by d.c. glow discharge of argon and using the target metal as a cathode. The accelerated

Table III. ESR Spin Concentration in Plasma Polymers and Glass Substrates.

Monomer	$C_s \times 10^{-19}$, spins/cm³		$C_g \times 10^{-15}$, spins/cm² *	
	Continuous	Pulsed	Continuous	Pulsed
C$_2$H$_2$	8.6	15.6	0	0
C$_6$H$_6$	3.2	1.6	0	0
C$_6$F$_6$	7.4	5.4	0	0
Styrene	3.8	0.54	0	0
C$_2$H$_4$	1.36	14.5	4.0	0.85
C$_2$F$_4$	13.0	8.4	11.2	1.8
Cyclohexane	0.84	0	1.1	0
Ethylene oxide	0.75	0.5	6.6	1.6
Acrylic acid	0.76	1.85	4.4	0
Propionic acid	1.0	1.0	6.3	1.6
Vinyl acetate	0.42	0.33	6.1	1.8
Methyl acrylate	0.31	0.15	6.4	1.5
Hexamethyldisilane	0.5	0.24	0	0
Tetramethyldisiloxane	0.49	0.05	0	0
Hexamethyldisiloxane	0.21	0	0	0
Divinyltetramethyldisiloxane	0.15	0.05	0	0
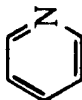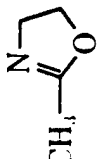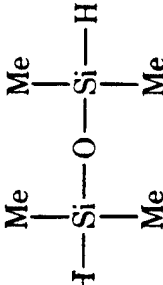
*Total spins divided by surface area of glass.

ions hit the target metal on the cathode and transfer the energy to the target atoms. The atoms, which receive energy from the impinging ions, shake up the structure and strike neighboring atoms. This energy transferring process ends up with some atoms leaving the solid phase and sputtering away into the gas phase. If a substrate material is placed in the gas phase, the sputtered material is deposited onto the substrate. This is one of the methods used to metallize polymer surfaces. Because the shake-up process occurs at the level of the atoms, alloys, such as stainless steel, can be used for sputter-coating, whereas metallization by evaporation cannot be used for alloys.

Glow discharge polymerization has many aspects in common with sputter-coating. Both processes are initiated by ionization of a gas (or vapors as in glow discharge polymerization). The major differences are the location of target material and the substrate. In the sputter-coating process, the target material is the cathode surface, and the substrate for coating is placed outside of the glow discharge. To avoid the effects of plasma, special efforts are often made to contain the glow discharge. For example, in a magnetron discharge, the superimposed magnetic field is used in the glow discharge polymerization, the target material is the monomer in a vapor phase, and the substrate is placed inside the glow discharge. The ionization process or collision of ions or electrons with molecules of the monomer "sputters" the fragments of the monomer molecules and deposits them on the substrate. Therefore, it may be assumed that both sputter-coating and glow discharge polymerization are atomic processes.

One of the unique characteristics of polymers formed by glow discharge polymerization is their strong tendency to exhibit internal (expansive) stress in the polymer layer during the process of deposition. When a thin layer of glow discharge polymer is deposited on a thin polymer film, the coated film tends to curl as a result of the internal stress in the coating. By knowing the thickness of both layers and the Young's modulus of the substrate film, the curling force and the internal stress can be calculated from the radius of the curled sample.[103] Typical cases are shown in Figure 26 and Table IV.

Table IV. Internal Stress of Plasma Polymer (thickness = 4000 Å; reaction conditions; 30 μm Hg monomer pressure and 80W power).

Monomer	Structure	σ_s, dynes/cm²
Thiophene		2.7×10^8
Pyridine		5.2×10^8
Acrylonitrile	$CH_2{=}CH{-}C{\equiv}N$	4.3×10^8
Furan		7.0×10^8
Styrene		4.3×10^8
Acetylene	$CH{\equiv}CH$	3.8×10^8
2-Methyloxazoline		0
Tetramethyldisiloxane		0
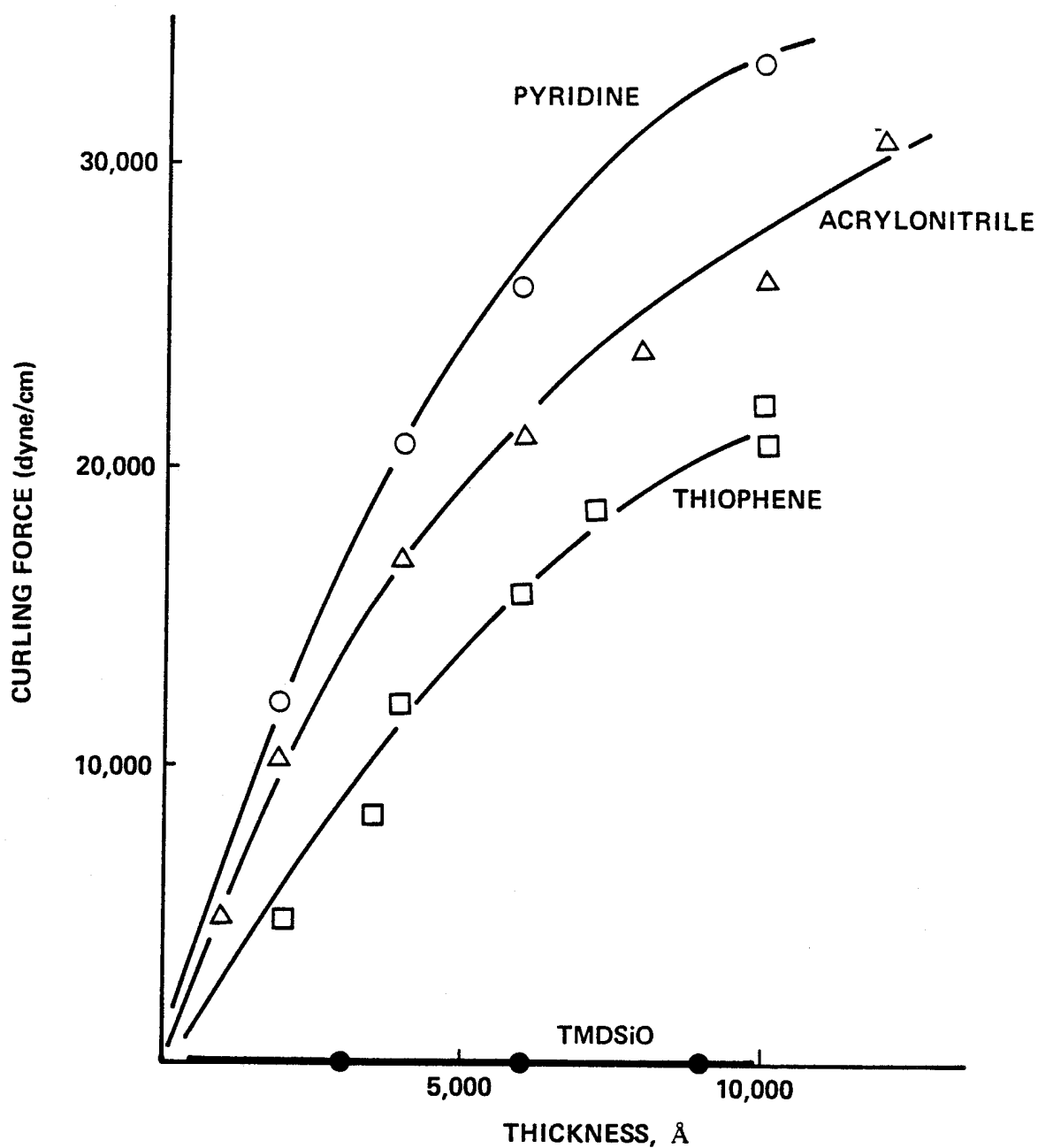
Figure 26. Curling force $\sigma_s d$, which is the product of the internal stress (σ_s) and the thickness (d) of the plasma-deposited layer, is plotted vs d. The three curves correspond to layers obtained by plasma polymerization of the indicated monomers.

This high level of internal stress sometimes causes self-distinction of the coating when too thick a layer is deposited. An important aspect is that the build-up of internal stress, manifested by the curling of the coated substrate, occurs during the process of polymer deposition. This aspect, therefore, should be directly related to the mechanism of polymer formation. Another possible cause of the internal stress is the absorption of oxygen by trapped free-radicals and subsequent absorption of water vapor by the oxygen containing functions. These two phenomena, which occur in general cases, will cause expansion or swelling of the polymer deposit. However, it has been found that there is no direct correlation between the free spin concentration observed in ESR and the reported internal stress. This indicates that the major portion of the build-up of internal stress occurs during the process of polymer deposition. This aspect is very similar to the stress build-up that takes place during the deposition of sputtered metal, thus indicating that the mechanisms is alike in both cases.

Polymers formed by glow discharge polymerization have much greater densities than coresponding conventional polymers.[104] For instance, the density of the glow discharge polymer of ethylene was found to be as high as 1.3, but the polymer has no crystallinity. The presence of high density and high expansive internal stress in the absence of crystallinity can be explained by the continuous impinging process in atomic polymerization, whereas the molecular polymerization mechanism offers no such reasonable explanation.

1.3.2.5 Structural Difference of Monomer and Polymer

The aspect of atomic polymerization can be clearly seen in the molecular structural difference of monomers and polymers, but with the glow discharge polymers of hydrocarbons, without appropriate analytical tools, it is difficult to demonstrate the difference in a (semi) quantitative manner, although such tests as elemental and infrared spectra analyses generally show that glow discharge polymers are quite different from corresponding conventional polymers. Specific analysis is hampered by the characteristic insolubility of most glow discharge polymers. However, the use of Electron Spectroscopy for Chemical Analysis (ESCA) to study the glow discharge polymers of perfluorocarbons provides a

unique opportunity to overcome these difficulties. The results of ESCA studies of glow discharge polymers of tetrafluoroethylene, $CF_2=CF_2$, are reviewed below in view of atomic polymerization.

Because of the strong electron negativity of fluorine atoms, the binding energy of the core level electron of carbon is shifted enough so that the amount of shift can be measured by the ESCA Cl_s spectrum. Consequently, ESCA can distinguish carbons that have one, two, or three fluorine atoms attached. Conventional polytetrafluoroethylene (Teflon) shows a singlet Cl_s peak, which corresponds to $-CF_2-$ at 291.5 e.v. This peak is shifted from the Cl_s peak of normal carbons (bound to H or C) at 284.5 e.v.

If a polymer is formed by plasma-induced polymerization in a glow discharge, the Cl_s peak should be a singlet at 291.5 e.v. as it is in the case of polytetrafluoroethylene. If a polymer is formed via a triple bond containing a precursor as it is proposed for the glow discharge polymerization of hydrocarbons, the Cl_s peak should be at a lower binding energy level (289 e.v.) than that for $-CF_2-$, because the formation of such a structure requies the abstraction of two fluorine atoms from two adjacent carbons to yield polymers with less fluorines. In the most typical cases, however, the Cl_s peak of the glow discharge polymer of tetrafluoroethylene contains a considerable amount of $-CF_3$, $-CF_2-$, and intermediate peaks in between $-CF_2-$ and C as shown in Figure 22. This strongly indicates that polymers are formed by neither molecular polymerization of the monomer nor (molecular) polymerization of the plasma-synthesized precursor. This situation is exactly what is to be expected of the atomic polymerization mechanism described earlier for plasma-state polymerization. (Namely M* can be a fragement of a molecule including a single atom).

Other evidence, which supports the concept of atomic polymerization, may be seen under certain conditions in the codeposition of aluminum (used as a substrate) in the glow discharge polymer of tetrafluoroethylene. When an excessive discharge power is used for the glow discharge polymerization of tetrafluoroethylene, the fluorine detachment and the consequent ablation prevail in the polymer formation. Under such a condition, the ESCA Cl_s peak indicates very little $-CF_3$, $-CF_2-$, and the

major peak becomes a broadened peak around 285.5 e.v. When this happens, the polymer deposition rate decreases drastically, and the ESCA spectrum shows the presence of Al as shown in Figure 27. The ESCA Al 2_s peak observed in this case is not identical to that of the Al foil used as the substrate, and the Fl_s peak also shows a conspicuous doublet, indicating that aluminum fluoride is formed and co-deposited in the glow discharge polymer.

1.3.2.6 Significance of Glow Discharge Polymerization

Atomic polymerization is not polymerization in the conventional sense, because the molecular structure of the monomers is not retained in the polymer. For instance, the glow discharge polymers of acetylene and benzene are very much alike. Their copolymerization characteristics are nearly identical. When N_2 and H_2O are added to benzene or acetylene, considering that one molecule of benzene is equivalent to three molecules of acetylene in glow discharge polymerization, nearly identical polymers are formed.[105] Yet, neither the glow discharge polymer of acetylene or benzene is quite the same as the glow discharge polymer of either methane or ethane. Therefore, the chemical structures of the monomers do play an important role in glow discharge polymerization, although the original structures or their derivatives may not be retained in the polymer structures. In this sense, absolute atomic polymerization can be seen in carbon films deposited from hydrocarbons when subjected to glow discharge. As shown in Figure 1, the overall glow discharge polymerization generally occurs by simultaneous atomic and molecular polymerizations.

If one accepts the concept of atomic polymerization as a mechanism of polymer formation in the glow discharge of organic compounds, little difference can be seen between the glow discharge polymerization and glow discharge deposition of inorganic materials, such as carbon, SN_x and Si. Thus, the true significance of glow discharge polymerization will be found in the preparation of entirely new materials, particularly hybrids of organic and inorganic materials rather than a method of polymerization in the conventional sense, which yields ill-defined polymers.
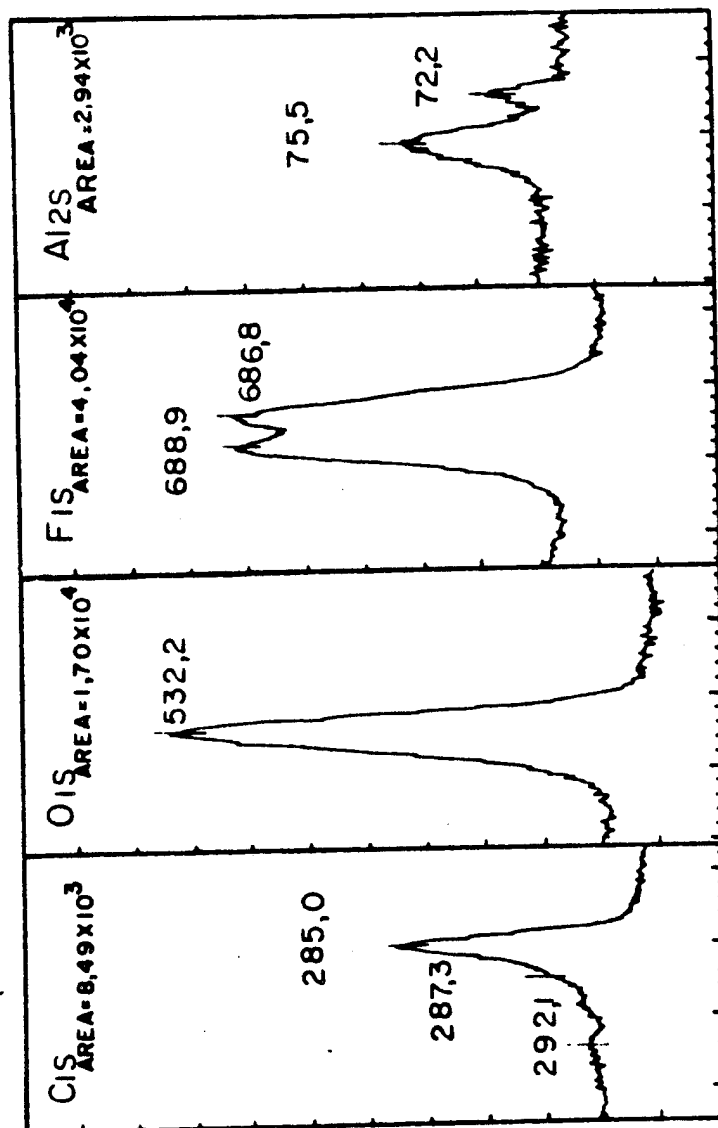
Figure 27. ESCA spectrum of glow discharge polymer of tetrafluoroethylene polymerized at high energy input (W/FM).

2.0 Report for December 1978 — November 1979

2.1 Introduction

The tasks for the final year of the contract were:

1) to modify the surface of polyvinylchloride tubing with glow discharge techniques alone or with glow discharge polymerization of tetramethyldisiloxane and to characterize the effects of these treatments on surface morphology and on the leaching of substrate components into water or saline under flexing and non-flexing conditions.

2) to establish the reproducibility of thickness, chemical composition and morphology of several replicate samples of tetramethyldisiloxane plasma polymer and submit samples coated in this manner for biological testing by NHLBI contractors. A similar program was carried out for TFE-2 plasma polymers. The latter utilizes tetrafluoroethylene monomer and is deposited under relatively high power conditions which result in a relatively fluorine-poor plasma polymer.

3) the effect of aging on the chemical composition of a plasma-polymerized tetramethyl disiloxane surface were studied.

The first task was carried out at the Research Triangle Institute while the second and third were undertaken by both the Research Triangle Institute and the University of Missouri-Rolla. The latter institution prepared samples for biological testing, and carried out studies of reproducibility of both TFE and TMDSiO plasma polymers, as well as an accelerated aging study of the latter. Because of RTI's access to infrared and ESCA spectra of better quality, the reproducibility of the chemical nature of tetramethyl disiloxane plasma polymer and the effect of aging on the latter were studied there as well.

In the following, results obtained at the two institutions will be presented separately, while the conclusions section draws on both sets of results.

2.2 <u>Research Triangle Institute Studies of Barrier Properties,</u>
<u>Reproducibility and Effect of Aging</u>

    2.2.1 <u>Infrared Absorption Characterization of Tetramethyldi-</u>
<u>siloxane Glow Discharge Polymers to Established Repro-</u>
<u>ducibility of Glow Discharge Polymerization and to</u>
<u>Detect Aging Effects</u>

The goals of the FTIR characterization of tetramethyldisiloxane
(TDMSiO) glow discharge polymers are:

1.   to define the differences in chemical character, if any, of
glow discharge polymer made by various preparative techniques
at RTI.

2.   to provide information regarding reproducibility of the TMDSiO
glow discharge.

3.   to demonstrate the effects of time on the chemical character
of the TMDSiO glow discharge polymer.

Items 1 and 2 are linked because a logical way to demonstrate
reprodubility in an IR spectrum is to determine that certain peak ratios,
which are extremely sensitive to preparative techniques, remain invariant
when a given preparative method is reproduced.

FTIR spectra have been obtained using the attenuated total reflec-
tion technique (ATR) for thin films (~ 1000 Å thickness). Films were
deposited on poly(vinylchloride) tubing or sheeting and spectra obtained
by pressing the coated side of the poly(vinyl chloride) against the
internal reflection element (IRE) used in ATR. Alternatively, the glow
discharge polymer film was deposited directly on the internal reflection
element (IRE).

The infrared absorption spectra previously available to us from
conventional instruments have typically shown broad absorption peaks and
have therefore contained limited information. This has been true regard-
less of whether the ATR technique or the usual transmittance methods
were used. Such spectra are seen in the first and second annual reports
for this contract (N01-HB-3-2913-1 and N01-HB-3-2913-2). The spectra
obtained using ATR and FTIR during this reporting year show sharp well-

defined peaks and therefore contain more information regarding the chemical content of the plasma polymers than previously available to us. They may be contrasted with the spectra obtained at the University of Missouri-Rolla using a conventional spectrometer (See Fig. 52), which are more typical of the quality of spectra attainable heretofore. In addition, the spectra at RTI are taken on plasma polymer films identical to those deposited on poly(vinylchloride) substrates, i.e., about 1000 Å thick and deposited on smooth surfaces, either the IRE or the poly(vinyl-chloride) itself. By contrast, any plasma polymer film used in conventional transmission measurements must either be much thicker than 1000 Å (if deposited on a NaCl plate) and/or deposited on a surface of very high area (if deposited on NaCl powder and pressed into a pellet as done at the University of Missouri-Rolla).

2.2.1.1 Experimental

FTIR spectra were obtained using the ATR technique and a Nicolet model 7199 infrared spectrometer. Internal reflection elements made of KRS-5 (thallium bromo iodide) were employed with an aperture angle of 45° for the glow discharge polymer deposited directly on the IRE, of 60° for plasma polymer deposited on polyvinylchloride. Single beam ATR spectra of glow-discharge polymer on PVC were ratioed against the single beam ATR spectrum for a PVC blank. This procedure is equivalent to running glow discharge polymer on PVC (ATR mode) in the sample beam and a PVC blank (ATR mode) in the reference beam in a conventional spectro-meter. The resultant absorption spectrum (Figure 28) would contain positive peaks for the glow discharge polymer and negative peaks for the PVC substrate (the sample beam sees less PVC than the reference beam). An absorption spectrum for PVC, multiplied by a factor, FCR, is added to spectrum 1 to eliminate the PVC negative peaks. The process is illustrated in Figure 28.

Single beam ATR spectra were obtained using 2500 scans and required 60-75 minutes per single-beam spectrum.

2.2.1.2 Results

TMDSiO glow discharge polymer was prepared at RTI by three preparative techniques. These are listed in Table V. The TMDSiO was obtained from PCR research chemicals in Gainesville, Florida and was used

Table V. TMDSiO Plasma Polymerization at RTI.

Procedure	Reactor	Position of RF Coil		Flow Rate $\frac{cm^3}{min}$ S.T.P.	Power (watts) p=pulsed	Pressure in Glow Discharge (millitorr)
		w.r.t. substrate	w.r.t. monomer flow			
1	Standard	upstream	monomer diffuses to coil	0.36	13	33
2	Narrow tube	downstream	monomer flows through coil	0.46	60p	30
3	Narrow tube	coil moves over substrate	monomer flows through coil	2	10p	22
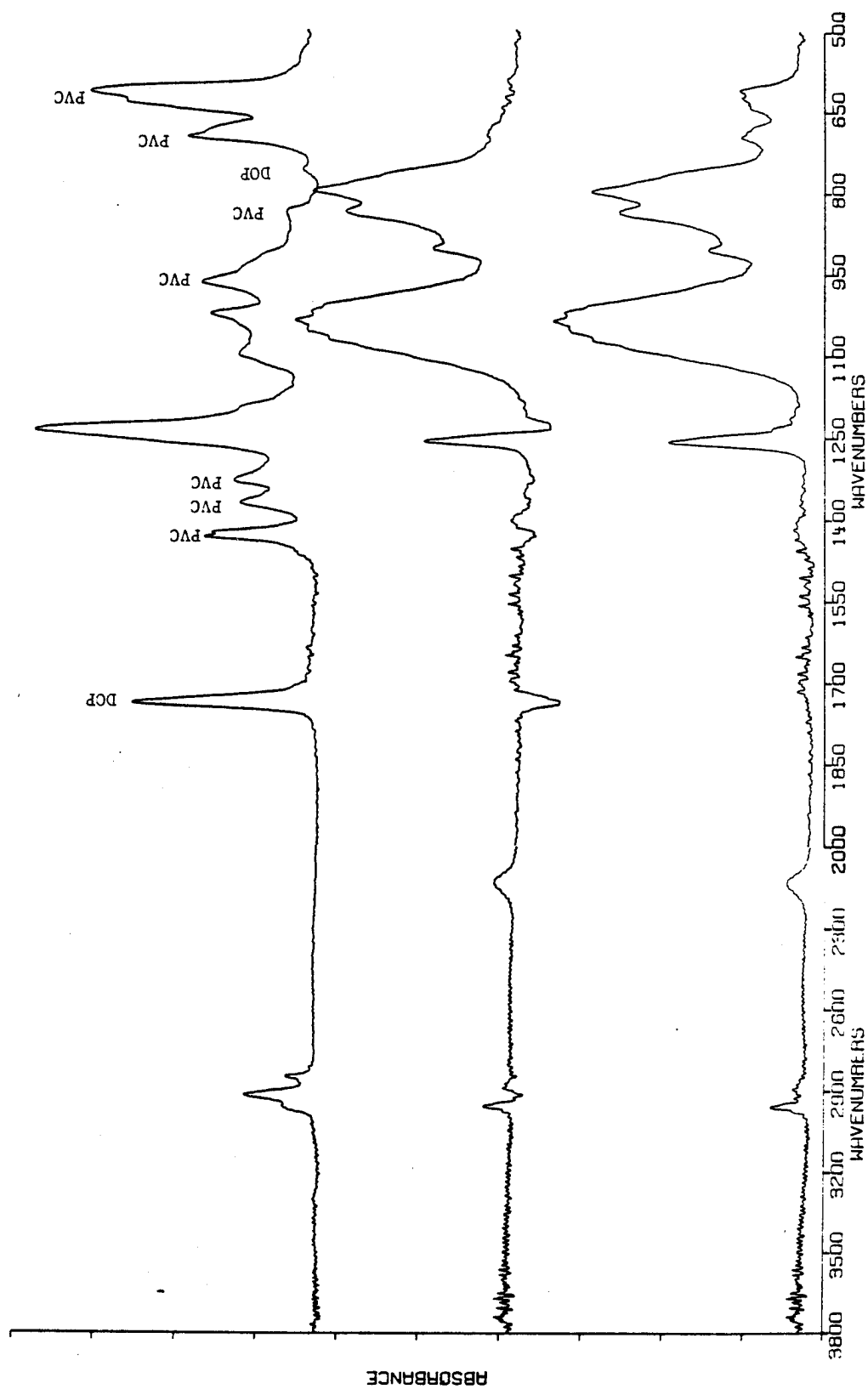
Figure 28. FTIR spectra obtained from tetramethyl disiloxane glow discharge deposited on a PVC sheet by procedure 1 (Table V). top: PVC spectrum, middle: glow discharge polymer on PVC ratioed against PVC, bottom: middle spectrum + a fraction of top spectrum to eliminate negative peaks.
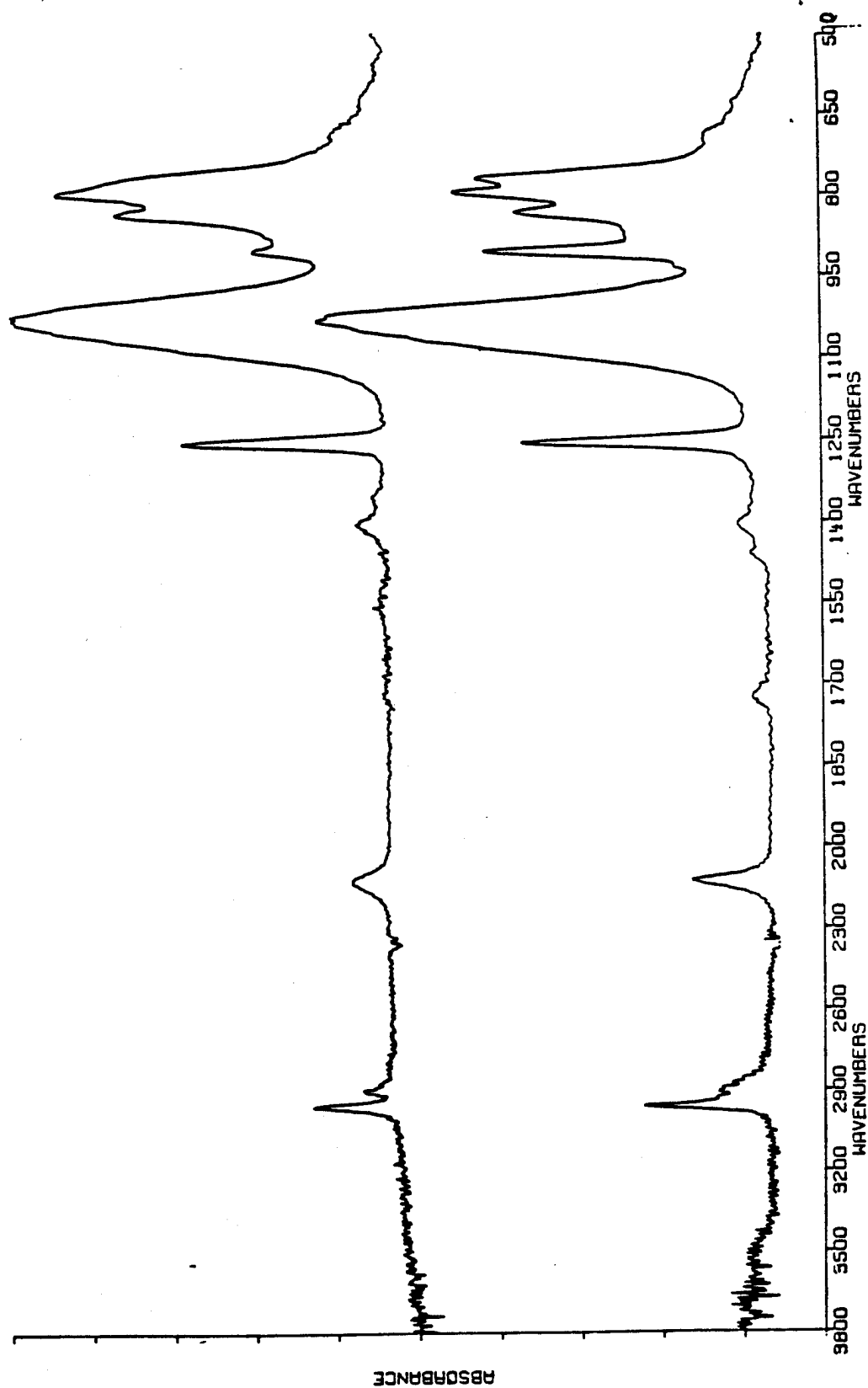
Figure 29. FTIR spectra obtained for 800 A of TMDSiO plasma polymer deposited on a KRS-5 internal reflection element using the attenuated total reflection (ATR) technique.
Top: Plasma polymer deposited in standard reactor using procedure 1 in Table V.
Bottom: Plasma polymer deposited in narrow tube reactor using procedure 2 in Table V.

as received. The FTIR absorbance spectra obtained using techniques 1 and 2 are shown in Figure 29 for deposition directly on a KRS-5 internal reflection element and in Figure 30 for all three techniques with glow discharge polymer deposited on poly(vinyl chloride).

The assignments made for the various peaks observed in the absorption spectrum of tetramethyl disiloxane glow discharge polymer are given in Table VI. The shape and location of the v_{as} Si-O-Si peak at about 1030 cm^{-1} is indicative of type of -Si-O-Si- chain.[113] For linear long chain siloxanes with three or more silicon atoms per run the band is clearly split into two components. In unstrained siloxanes the single peak is at 1060-1090 cm^{-1}, whereas shifts to longer wavelengths occur in strained structures such as hexamethyl cyclotrisiloxane and other cyclic siloxanes. The single peak at 1030 cm^{-1} therefore indicates the lack of long linear segments of the type $(Si-O)_n$. This is reasonable as the Si/O ratio in tetramethyl disiloxane is twice that required for long linear siloxane chains. In addition the position of the peak indicates a strained Si-O-Si bond.

The most obvious changes in the infrared spectra for various reaction conditions are in the group of peaks between 950 cm^{-1} and 740 cm^{-1}. The four peaks that are observed are listed in Table VI. Attempts to synthesize the observed profiles using a curve analysis program reveal an additional peak at about 870 cm^{-1}. The peak at 905 cm^{-1} is attributed to Si-H bond. The other four peaks at 870, 840, 800 and 770 cm^{-1} are attributed to rocking of methyl groups attached to silicon. The number of methyl groups attached to the silicon atom affects the location of the rocking band(s). Thus a single methyl group absorbs at 763 cm^{-1} (weak), two methyls at 855 and 800 cm^{-1} (medium) and three methyls at 840 (strong) and 763 cm^{-1} (weak).[108,112,115] The relative intensities of absorption are taken from Smith's table of infrared spectra structure correlations.[112] A peak at 770 cm^{-1} is also attributed to the asymmetric Si-C-Si stretch in $SiCH_2Si$. This group should also yield a strong peak in the 1000 cm^{-1} - 1100 cm^{-1} region and a weak peak at 1350 cm^{-1}. However the peak at 1000 - 1100 cm^{-1} can be swamped by the Si-O-Si peak in the same region.[115] Notwithstanding the above correlations, tetramethyl-disiloxane in the liquid phase is observed to have three peaks at 880 cm^{-1} (very strong, ρCH_3), 832 (strong, ρCH_3) and 770 (strong, $\rho_{as} SiCH_2$)[110]

Table VI. Assignment of IR Absorbance Bands for Tetramethylsiloxane Glow Discharge Polymer.

Band (cm^{-1})	Assignment	Reference	Intensity in Plasma Polymer Spectrum
3680	ν OH	106	Absent
2960, 2870	ν CH	107	Medium
2140	ν SiH	108	Medium
1715	ν C=O	107	Weak
1625	ν C=C in Si-C=C	109	Weak
1460	δ_s CH_2, δ_{as} CH_3 ($SiCH_2CH_3$)	107,115	Weak
1410	δ_{as} CH_3 (S-CH_3)	110,115	Weak
1385	$\delta_s CH_3$ (Si-CH_2-CH_3)	115	Weak
1355	δCH_2 (Si-CH_2-Si)	111,112,115	Weak
1250	$\delta_s CH_3$ (Si-CH_3)	108	Strong, sharp
1030	ν_{as} Si-O-Si ωCH_2[Si$(CH_2)_n$Si]	113	Strong
905	ρ SiH	110,112	Strong, sharp
840	ρ Si$(CH_3)_3$	112	Strong, sharp
800	ρ Si$(CH_3)_2$ (also at 860)	112	Strong, sharp
770	ρ Si$(CH_3)_3$ + SiCH$_3$ Si(CH_2)-Si	112	Strong, sharp

(Between 1460 and 1355 rows, bracketed annotation: δCH_2, (Si-CH_2 | CH_2 | Si))
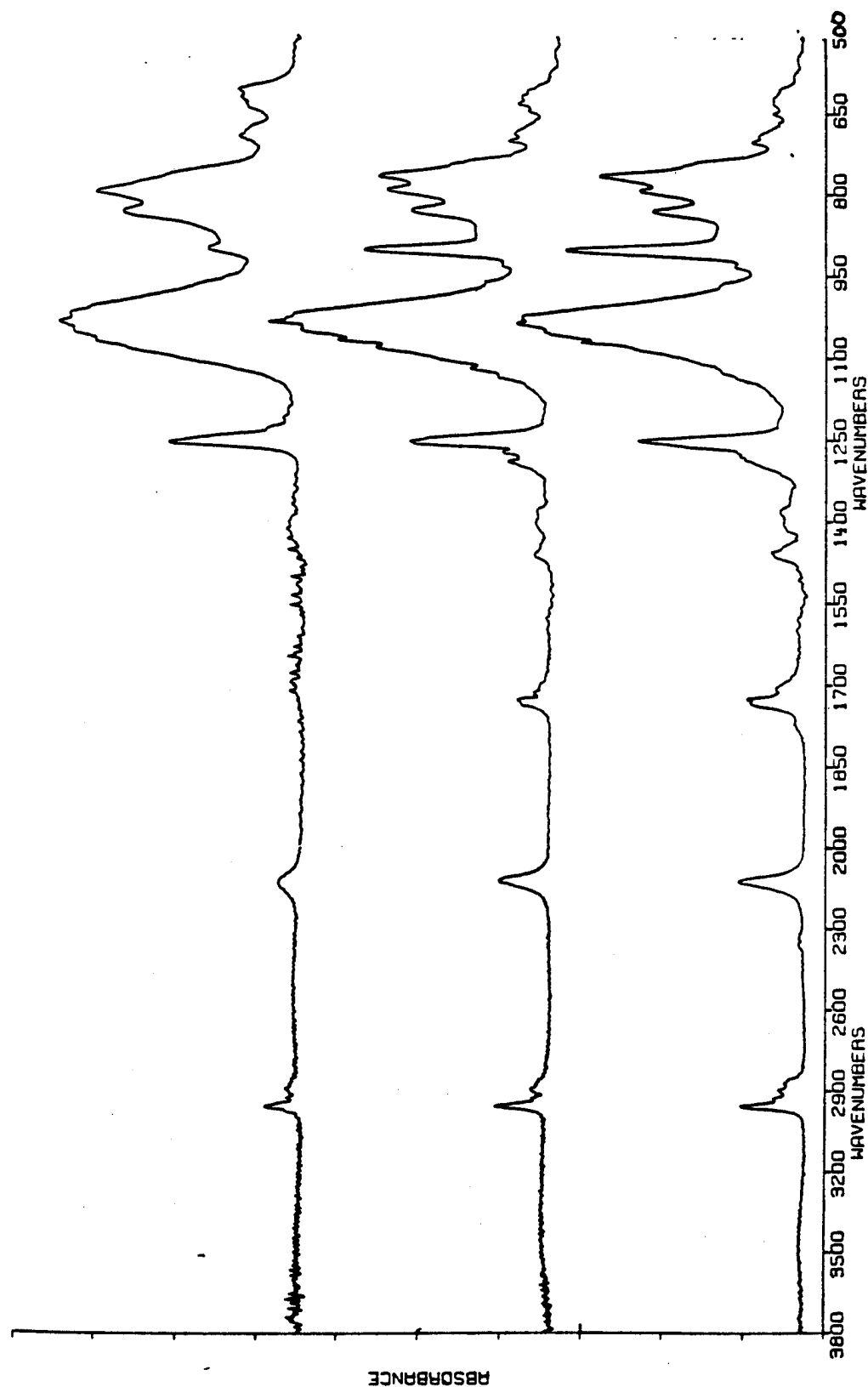
Figure 30. FTIR spectra obtained for 1000 Å of TMDSiO plasma polymer deposited on PVC. Spectra are obtained by the ATR technique with plasma polymer surface pressed against a KRS-5 internal reflection element.
Top: Plasma polymer deposited on PVC sheet in standard reactor (procedure 1 in Table V).
Middle: Plasma polymers deposited inside PVC tubing in narrow tube reactor with stationary coil (procedure 2 in Table V).
Bottom: Plasma polymer deposited inside argon plasma treated PVC tubing with moving coil (procedure 3 in Table V).

(See Figure 31). The correlations are more faithfully followed for linear methyl oligo- siloxanes[114] and polydimethylsiloxane,[111] both with very intense peaks at 800 cm^{-1}.

The group of peaks between 1460 and 1355 cm^{-1} can be attributed to a variety of methylene and methyl groups including $Si-CH_3$, $Si-CH_2-CH_3$ and $Si-CH_2-Si$ as indicated in Table VI. The Si-H stretch at 2150 cm^{-1} has been shown to be sensitive to the inductive power of other groups on the silicon atom, the more electron withdrawing groups causing shifts to higher frequencies.[116] It should also be noted that the Si-Si vibration is usually inactive in the infrared.[112]

Peak area ratios were used to ascertain the reproducibility of procedure 2 in Table V as well as the effect of aging for procedure 1 and 2.

2.2.1.2.1 Reproducibility of Chemical Nature of Glow Discharge Polymer by IR

Spectra obtained for four replicate depositions of tetramethyldisiloxane glow discharge polymer by means of the procedure 2 (narrow tube reactor, stationary coil, see Table V) are shown in Figure 32. In all of these experiments a poly(vinyl chloride) tube was located in the center of the narrow tube reactor (see Figure 45), so the results reflect the chemical nature of the glow discharge polymer deposited on PVC tubing and used in the leaching studies described in Section 2.2.3 For spectra a-c, a 50 x 5 x 2 mm internal reflection element was placed in the middle of the poly(vinyl chloride) tube. For spectrum a in Figure 32, the glow discharge polymer was deposited inside the tubing. A 50 mm long piece of tubing was then cut from the center of the tube and its inside surface was pressed against a 50 x 10 x 2 mm IRE in order to obtain an infrared absorption spectrum.

The spectra for plasma polymer deposited on IRE (a-c in Figure 32) are very similar to those for plasma polymer deposited directly on the Tygon tubing. The principal differences are in the shape of the peak at 1720 cm^{-1}, at 1250 cm^{-1} and in the addition of two new peaks at 695 cm^{-1} and 620 cm^{-1}. The peak at 1720 cm^{-1} is a carbonyl peak and is present in the spectrum of PVC (Tygon tubing) because of dioctylphthalate
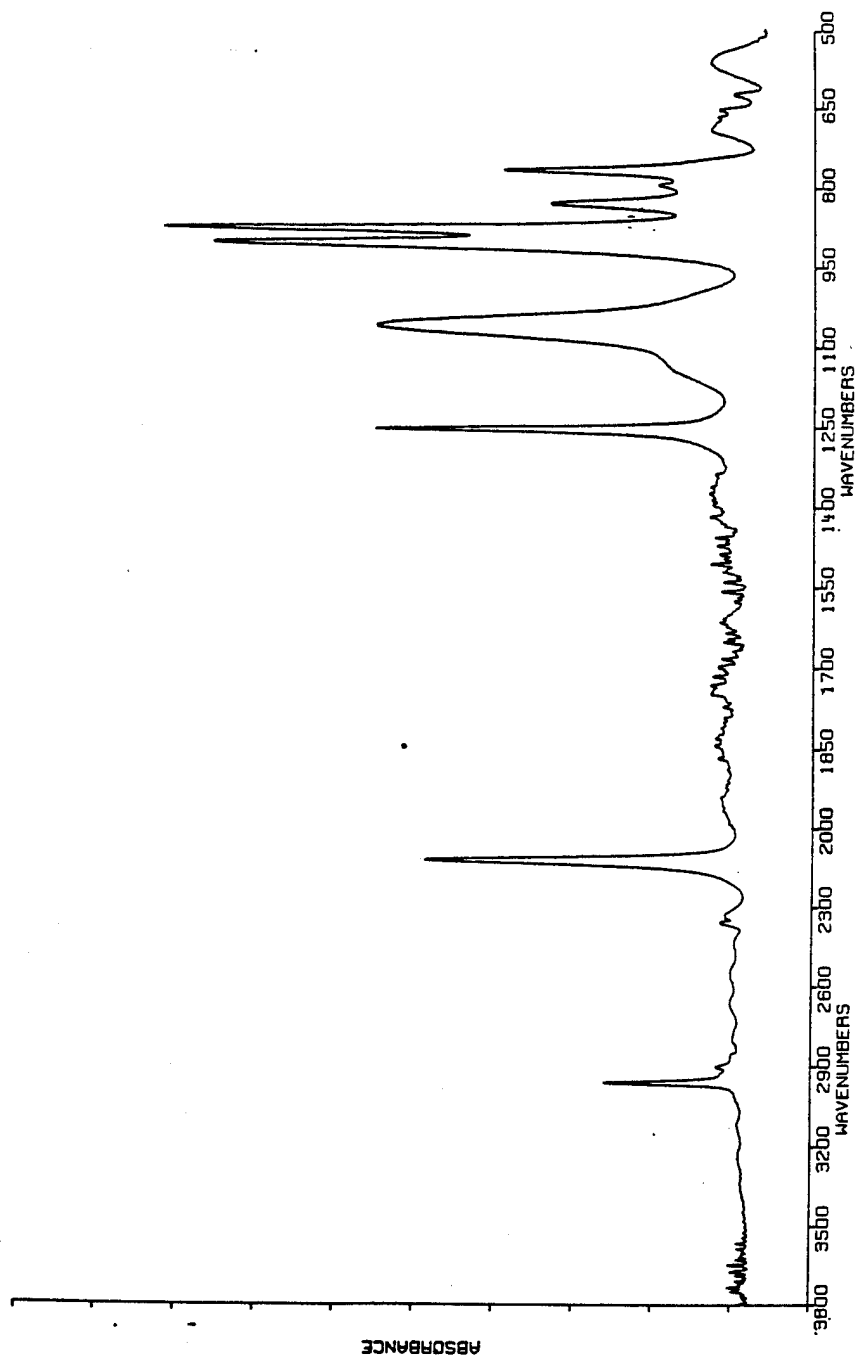
Figure 31. FTIR spectra obtained for tetramethyldisiloxane monomer in liquid cell.
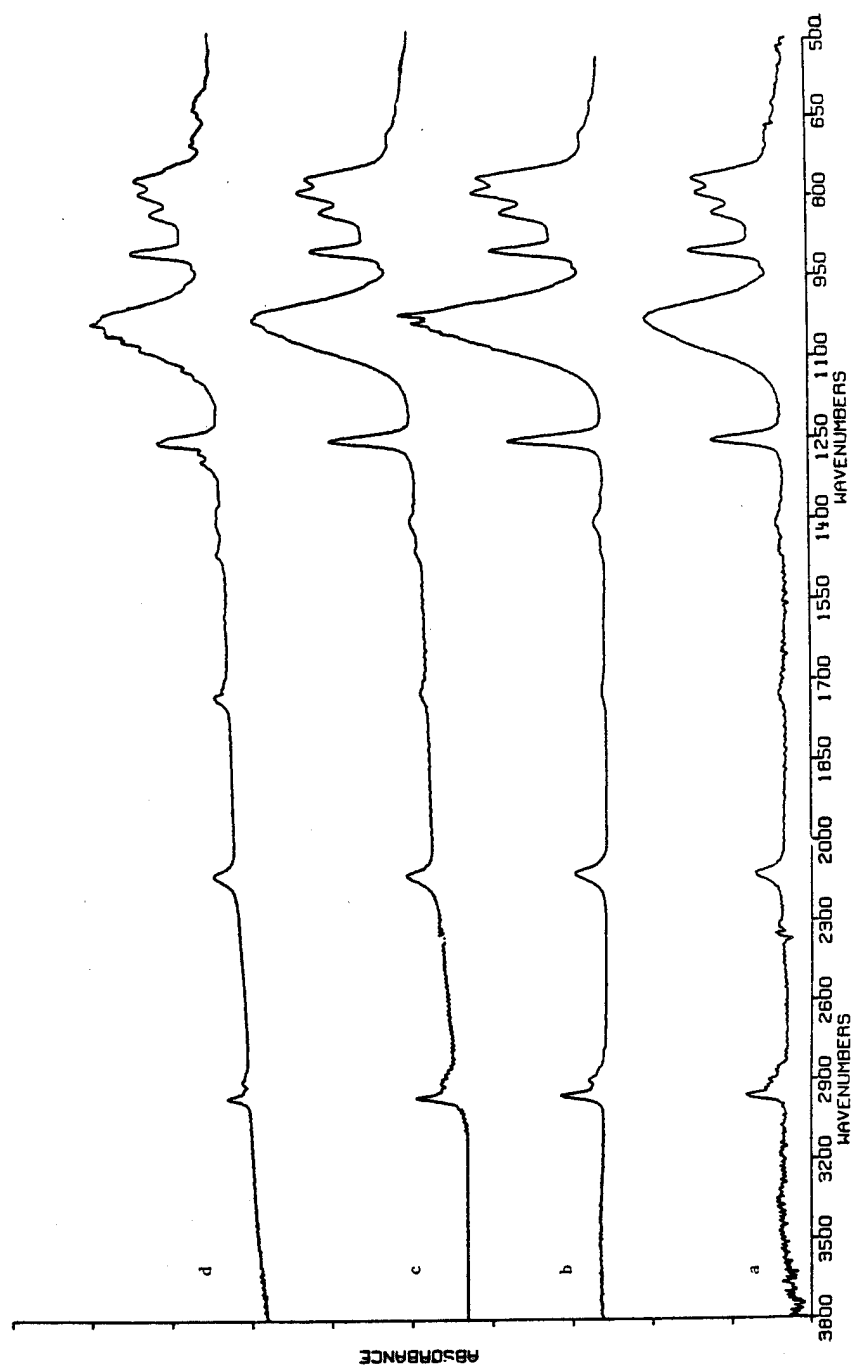
Figure 32. FTIR spectra obtained by means of the ATR technique of tetramethyldisiloxane glow-discharge polymer deposited by means of procedure 2 (see Table V) in replicate preparations a, b, c, on a KRS-5 internal reflection element placed inside a PVC tube and d.) on PVC tubing.

plasticizer (DOP).[117] In fact the two strongest peaks in the PVC spectrum (see Figure 42) are at 1720 cm^{-1} and 1290 cm^{-1} both attributed to DOP. In addition both show shifts in going from the neat phase to association with plasticized PVC.[117] It has also been shown that changes in conformation of the PVC chain will change the location and intensity of the C-Cl peak at about 690 cm^{-1}.[117] Finally intense peaks are present at 638 and 604 cm^{-1} for crystalline PVC. Thus the changes noted may be due to changes in the morphology of the PVC near the glow discharge polymer Tygon tube interface and in the degree of association of DOP with PVC. An alternative explanation for the peaks at 695 and 620 cm^{-1} is that some chlorine from PVC has been incorporated in the glow discharge polymer in C-Cl and Si-Cl bonds, respectively.

Peak areas were obtained for the more intense peaks in the spectra and are presented as ratios with respect to the Si-O-Si peak at 1030 cm^{-1} in Table VII. The peak areas for the peaks at 1030 cm^{-1}, 800, 870, 840 and 770 cm^{-1} were obtained with the aid of a curve synthesizer program.

The use of the curve synthesizer is illustrated in Figure 33 for curve c in Figure 32. The upper curve is experimentally observed, the middle curve is the synthesized curve, and the bottom curves are the individual components of the synthesized curves. The curve analysis program allows one to vary line shape (relative amount of Gaussian and Lorentzian shape) peak location, height and width. It was found that 75% Gaussian shape yielded the best fit to the 1035 cm^{-1} peak and this shape was used throughout. For the 835, 800 and 770 cm^{-1} peaks the additional restriction that all three peak widths must be identical was used in fitting the synthesized profile to the spectrum. Minor peaks were added after the best possible fit was achieved for the four major peaks.

The peak area ratios involving methyl groups on Si are plotted in Figure 34. The results in the last column should be ignored as these deal with the change in the spectrum obtained on IRE 3 as a function of time (to be discussed later). The greatest variability in the ratio is for the peaks at 2900, 1250 and 870 cm^{-1}. The variations in the peak

Table VII. Infrared Peak Area Ratios for Tetramethyldisiloxane Glow Discharge Polymer (All Peak Areas Divided by that of Peak at 1030 cm^{-1}).

Procedure[1]	Sample Designation (TMDSiO on)	Infrared Absorption Peak								
		Si-H				Si-(CH$_3$)$_x$ (x = 1-3)				
		905cm^{-1}	2140cm^{-1}	2900cm^{-1}	1250cm^{-1}	870cm^{-1}	840cm^{-1}	800cm^{-1}	770cm^{-1}	Σ^2
2	Tygon Tubing	0.135	0.104	0.080	0.153	0.060	0.136	0.162	0.178	0.54
2	IRE-1	0.136	0.116	0.168	0.103	0.060	0.136	0.162	0.178	0.54
2	IRE-2	0.133	0.117	0.132	0.115	0.057	0.161	0.195	0.193	0.606
2	IRE-3	0.131	0.114	0.180	0.112	0.101	0.136	0.181	0.162	0.58
2	IRE-3 (after 153 days)	0.078	0.024	0.087	0.078	0.036	0.094	0.200	0.058	0.39
1	PVC Sheet	0.051	0.059	0.059	0.118	0.078	0.187	0.219	0.127	0.61
1	IRE	0.088	0.061	0.112	0.107	0.045	0.209	0.239	0.159	0.65
1	IRE (after 155 days)	0.065	0.024	0.089	0.083	0.015	0.163	0.234	0.085	0.50

1 See Table V

2 Σ = 770 + 800 + 840 + 870.
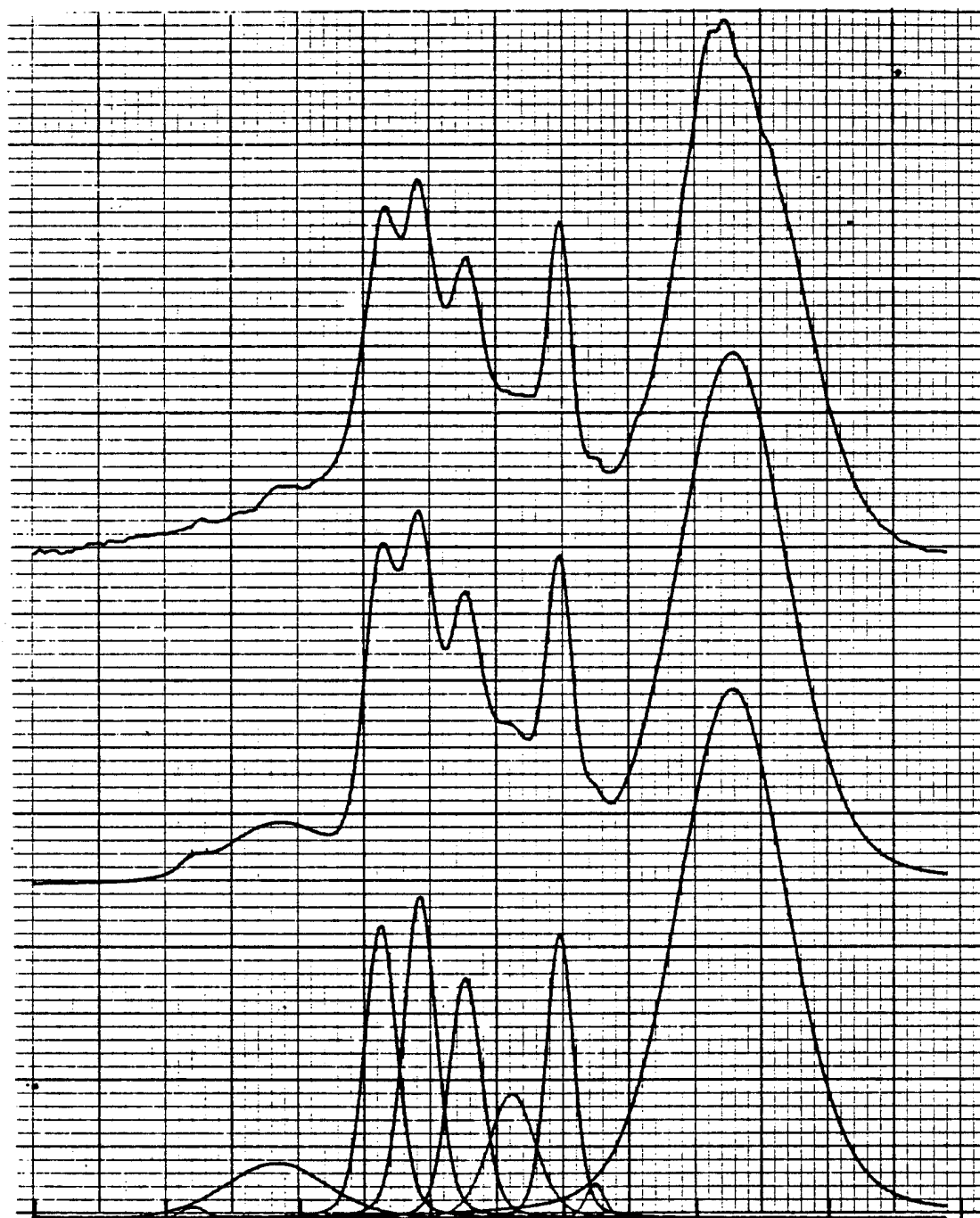
Figure 33. Curve analysis procedure applied to a portion of bottom
curve of Figure 29. The top curve is the experimentally
observed curve; the middle curve is the synthesized curve;
the bottom line shows the individual components that yield
the synthesized curve. The spectrum is in the opposite
sense to that shown in Figure 29, i.e., here the wavenumbers
increase from left to right.

Figure 34. Infrared absorbance peak area ratios for replicate preparations of TMDSiO glow discharge polymer by procedure 2 and effect of aging. All peak areas are divided by that of the 1030 cm^{-1} peak (Si-O-Si) and are indicative of methyl groups.

ratio for the 2900 peak on Tygon tubing as opposed to that on the IREs is undoubtedly related to the fact that a 2900 group of peaks is also present in the Tygon tube spectrum and small errors in the data processing to remove Tygon peaks from the composite Tygon glow discharge polymer spectra can lead to large errors in peak area. The variability amongst the IRE 2900/1030 peak area ratios appears to be related to signal to noise ratio. The 2900 peak is in the noisiest part of the spectrum and the peak height ratio appears to be higher for the two spectra with somewhat poorer signal-noise ratios at 2900 cm^{-1}. The 1250 cm^{-1} peak also shows poor agreement on going from PVC to the IRE spectra. However the shoulder on the 1250 cm^{-1} peak for the spectrum on PVC has already been noted and attributed to DOP in the Tygon tubing. Without this interference the agreement between peak height ratios, 1250/1030 cm^{-1} for the three IRE's is excellent. The 870 cm^{-1} peak is the last one to be fitted in the curve synthesis procedure so the poor agreement for the 870/1030 cm^{-1} peak ratios is hardly surprising. The peak ratios remaining involve the three peaks at 870, 840, 800, and 770 cm^{-1} which make up a composite peak. Agreement between the four replicate preparations appear to be affected more by the uncertainty in fitting peaks to the composite spectra than in chemical differences between the glow discharge polymers. Thus if one plots the ratio of the sum of the 870, 840, 800 and 770 peak areas to the 1030 cm^{-1} peak area as seen in Figure 35, excellent agrement among the replicate preparations is observed.

Peak area ratios for Si-H peaks divided by the Si-O-Si 1030 cm^{-1} peak area are shown in Figure 36. Excellent agreement is achieved between the four replicate preparations.

Mean value and standard deviations for the peak area ratios discussed are given in Table VIII. The excellent agreement obtained for the 1250/1030 the [800 + 840 + 770 + 870)/1030], the 905/1030 and 2140/1030 peak area ratios may be noted. The standard deviations for these ratios is 6% or better. The poor agreement for the 870 cm^{-1} peaks need be of no concern. The poorer than normal agreement for the

Table VIII

Infrared Peak Area Ratios for Replicate Preparations of

Procedure 2 [Ratioed to 1030 cm^{-1} Peak]

Location of Peak (cm^{-1})

	2900	1250	800, 840, 770, 870	800	840	770	870	905	2140
For IRE only	0.16	0.11	0.58	0.18	0.14	0.18	.073	0.133	0.116
Std. Dev. (%)	16	6	6	9	10	9	34	3	1
For Deposition on IRE and PVC			0.57	0.175	0.14	0.18	0.053	0.134	0.113
Std. Dev. (%)			6	9	9	7	22	2	5
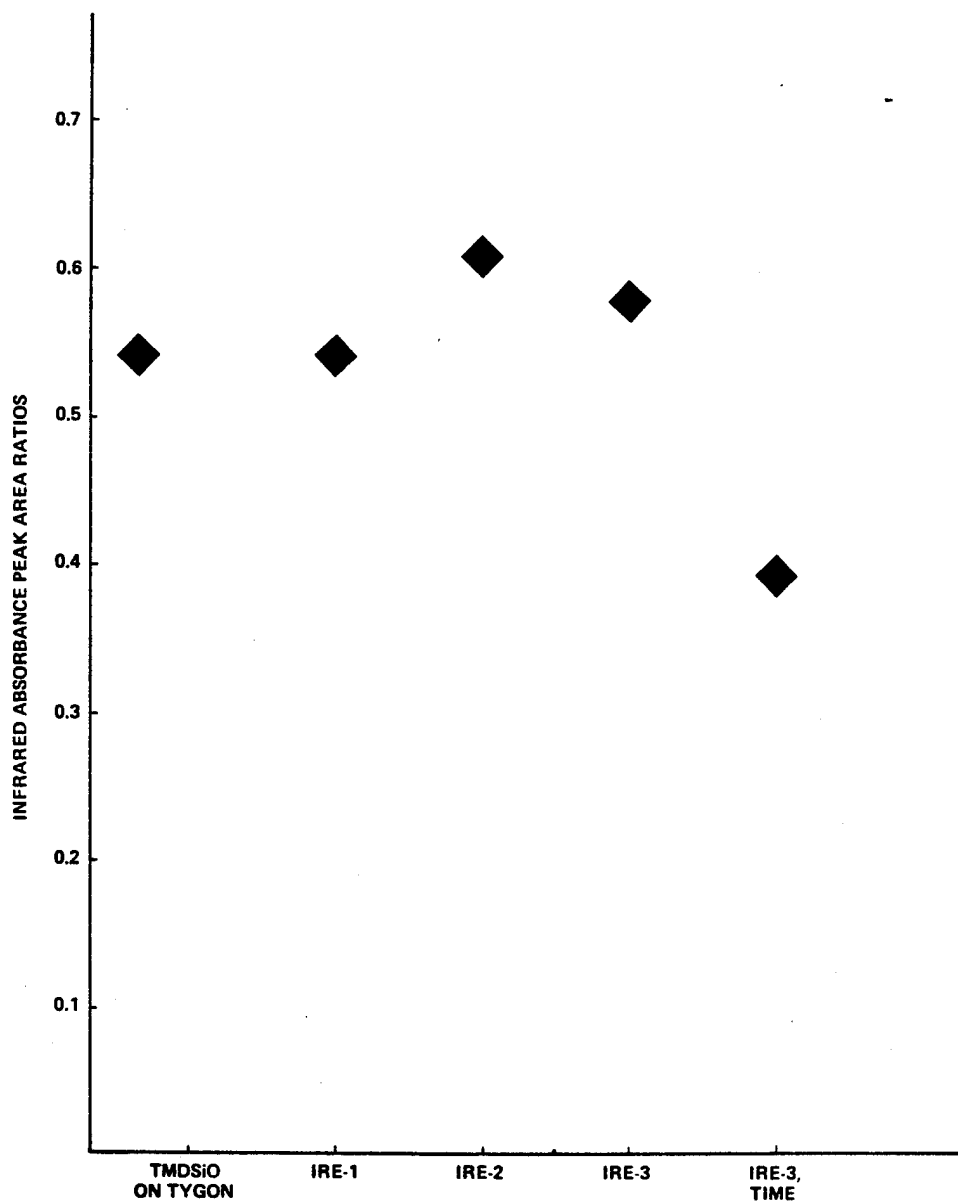
Figure 35. Area of composite (870,840,800 and 770 cm^{-1}) peak divided by
that of the 1030 cm^{-1} peak (SiOSi) for replicate preparations
(procedure 2) and effect of aging. All peaks in the composite
peak are indicative of methyl groups bonded to silicon (Si-CH$_3$).
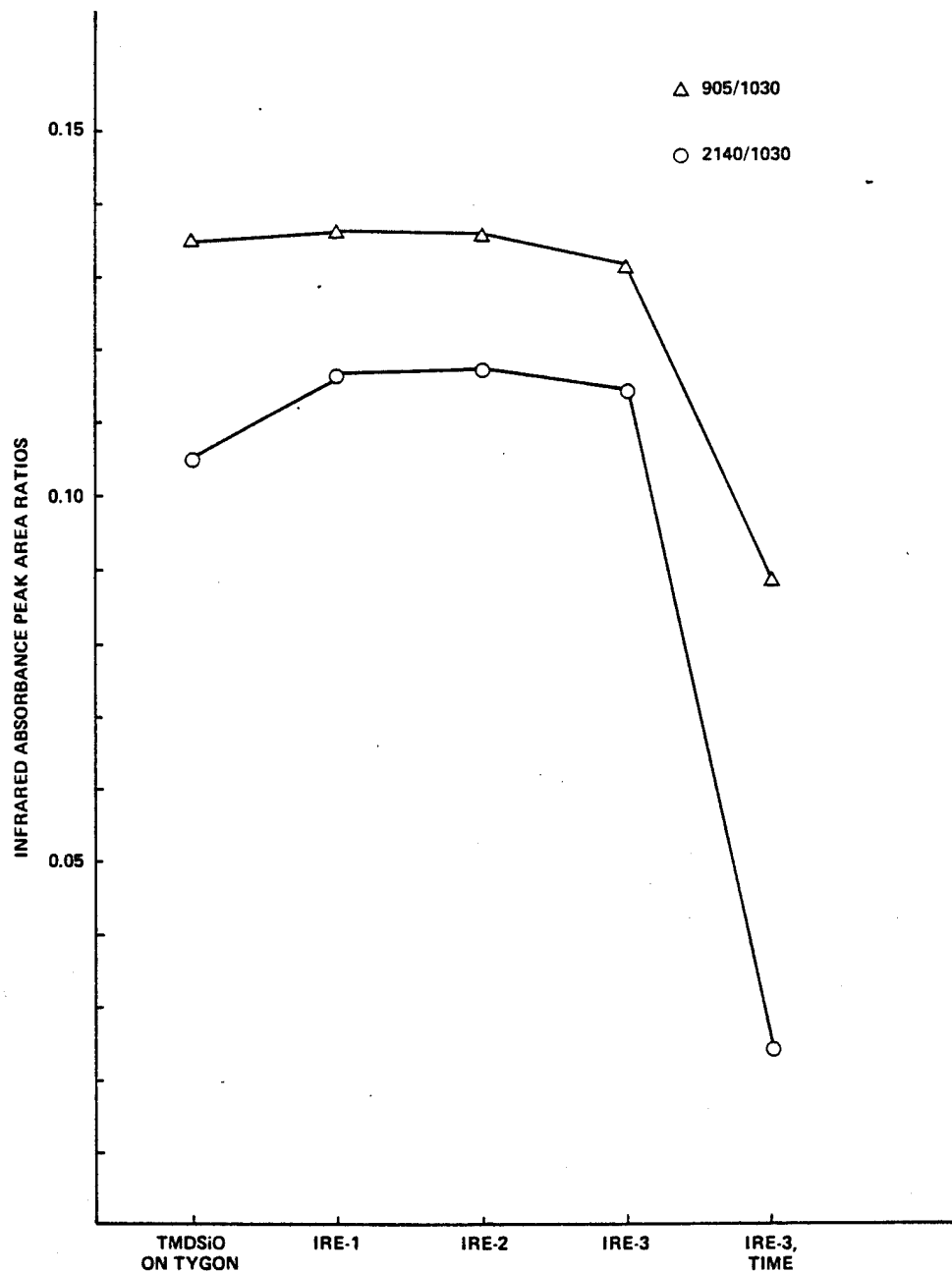
Figure 36. Infrared absorbance peak area ratios for replicate preparations of TMDSiO glow-discharge polymer by procedure 2 and effect of aging. The peaks are indicative of $Si-H$ groups and peak areas are divided by that of the 1030 cm^{-1} peak (Si-O-Si).

2900 cm^{-1} peak appears to be related to poor signal/noise ratio. For all other peaks the standard deviation is better than 10%, 40% of which may be attributed to errors in fitting individual peaks to the composite peak in the curve synthesis procedure.

Tetramethyldisiloxane glow discharge polymer was also deposited by means of procedure 1 on a polyvinyl chloride sheet and also on an IRE in the absence of PVC. The spectra are shown in Figures 29 and 30. Peak area ratios are given in Table VII and Figures 37-39. Again the last column in the figure should be ignored as it deals with spectra obtained after aging. The agreement between the spectra on IRE and on PVC seems somewhat better than for Tygon tubing. The sheet is less flexible than the tubing and the infrared spectrum (see Figure 28) for the PVC sheets shows PVC peaks more prominent with respect to DOP peaks than was the case for Tygon. The differences at 1250 cm^{-1} and 1700 cm^{-1} which were noted for procedure 2 are not noted between IRE and PVC for procedure 1. As a result there is excellent agreement in the $1250/1030$ and composite $[(860 + 840 + 800 + 700)/1030]$ peak height ratios between PVC and IRE. There is also good agreement between the $2140/1030$ peak height ratios but this is not the case for $905/1030$ cm^{-1}. It may be noted that the 905 cm^{-1} peak is considerably smaller with respect to its neighbors for procedure 1 than procedure 2 so that the apparent lack of reproducibility in this case is again related to errors in the curve synthesis procedure.

The peak height ratios for the two procedures indicate that procedure 1 yields a polymer with a greater concentration of $Si(CH_3)_2$ and $Si(CH_3)_3$ but less Si-H and $Si(CH_3)_1$. These relative concentrations can be manipulated by varying power, flow rate and pressure.

2.2.1.2.2 Aging of Tetramethyldisiloxane Glow Discharge Polymer

Two of the IRE's coated with glow discharge polymer (one procedure 1, one procedure 2) were allowed to age under ambient conditions with repeated analysis by ATR FTIR. The spectra obtained are shown in Figure 40 and 41. Peak area ratios for the longest aging times available for each procedure are included in Figures 34-39. For procedure 1 the most obvious changes by inspection are in the growth of a peak at 1700 cm^{-1}
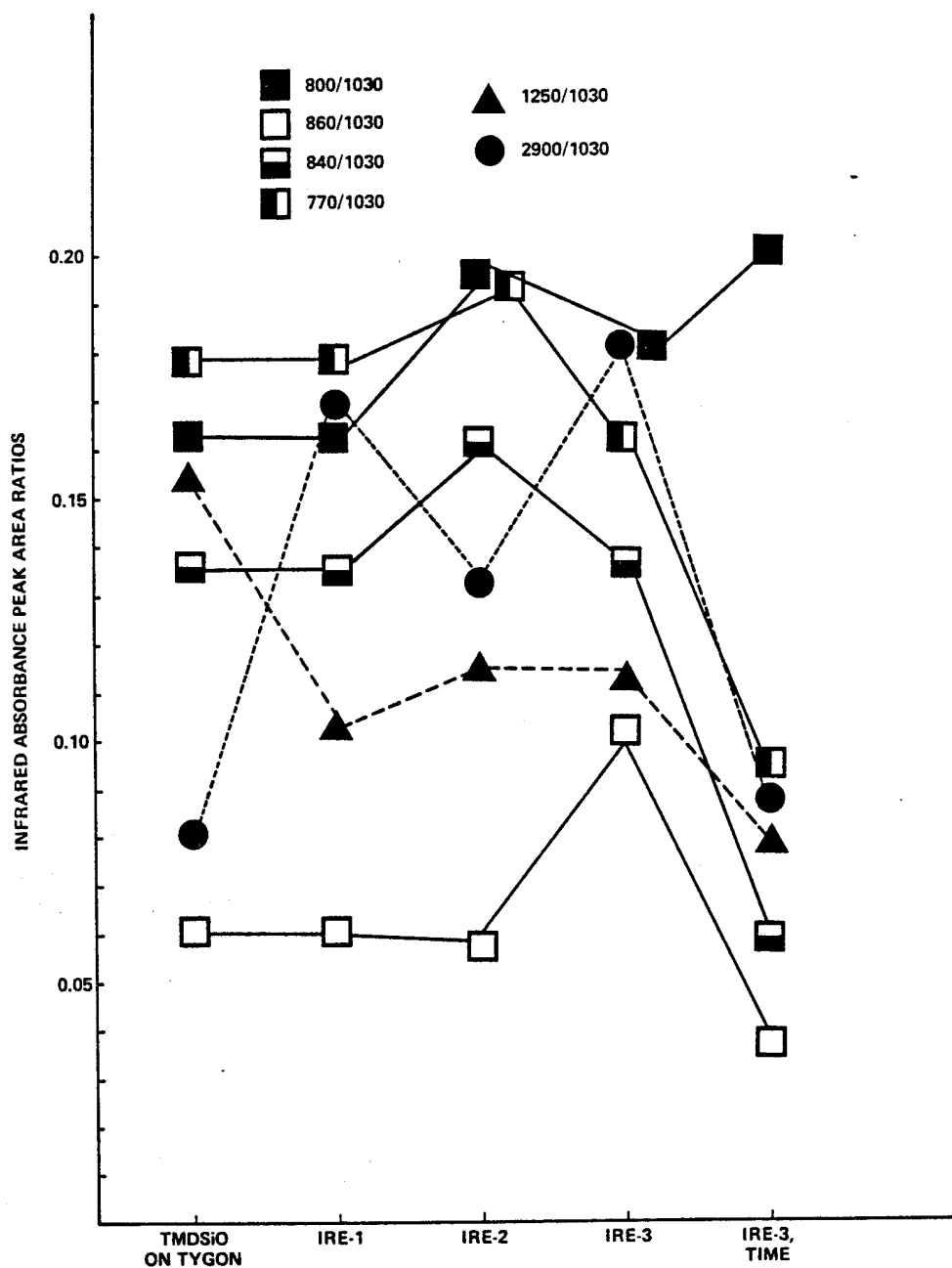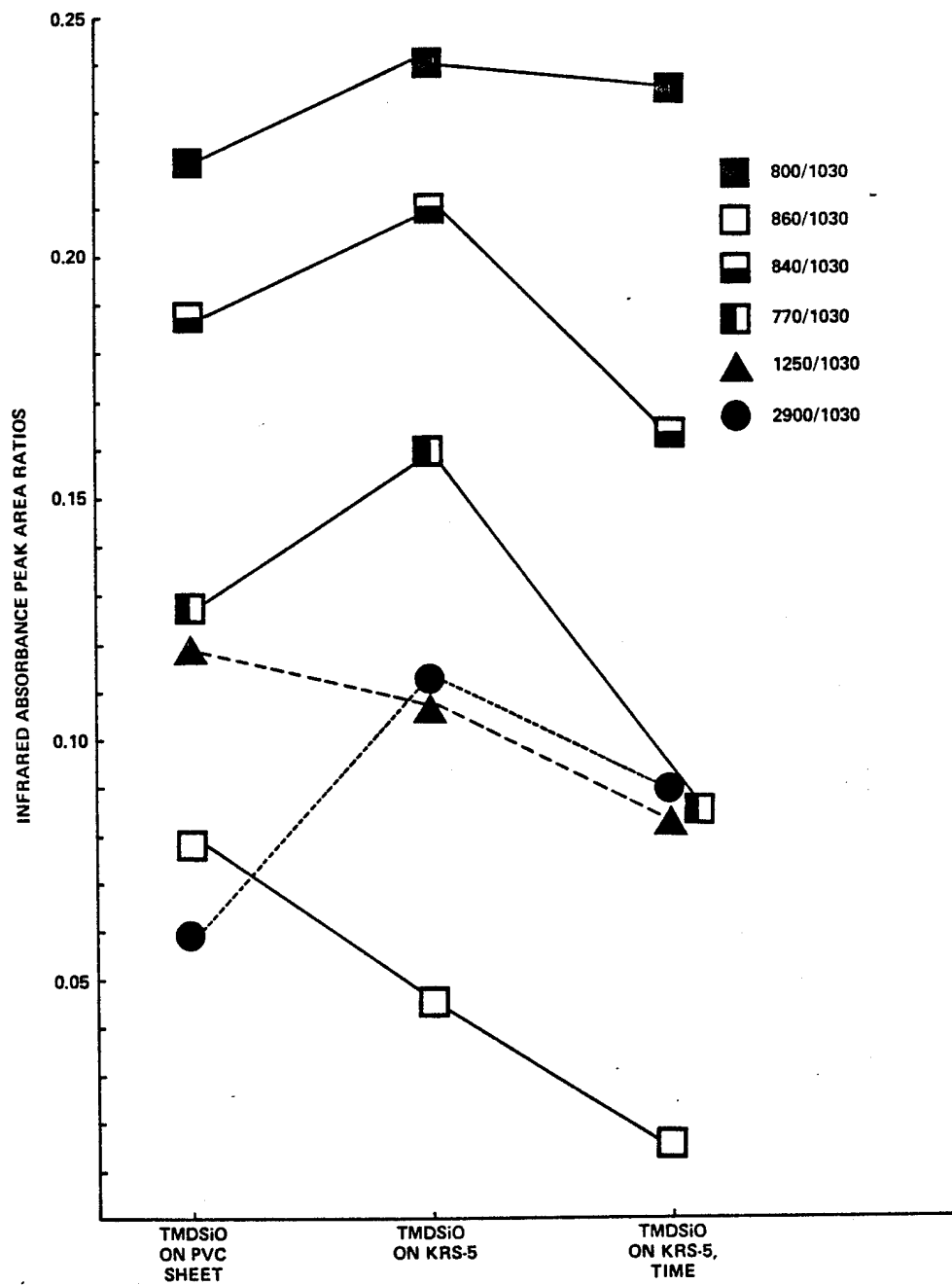
Figure 37. Infrared absorbance peak area ratios for replicate preparations of TMDSiO glow-discharge polymer by procedure 1 and effect of aging. All peak areas are divided by that of the 1030 cm^{-1} peak (Si-O-Si) and are indicative of methyl groups.
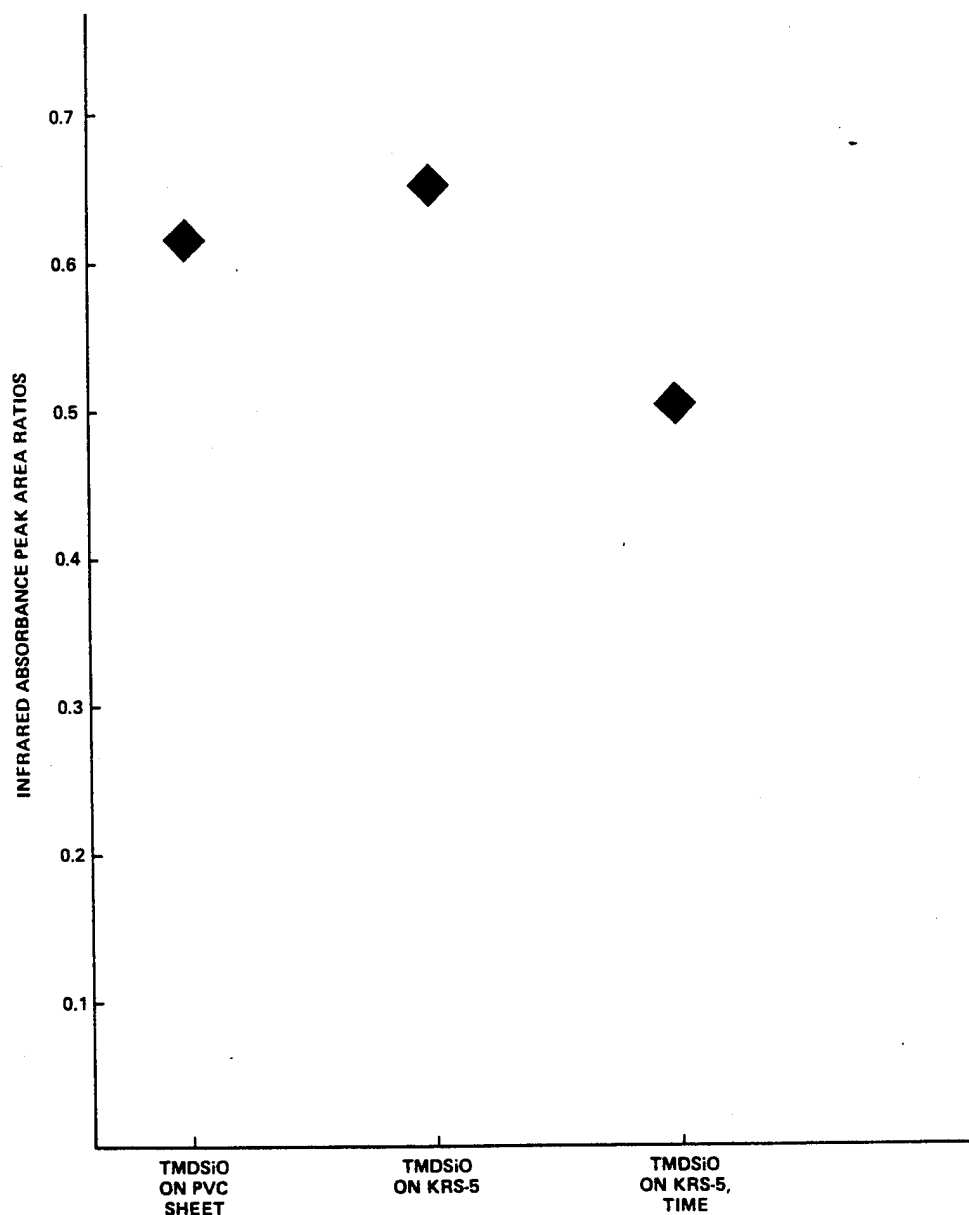
Figure 38. Area of composite $(870, 810, 800$ and 770 cm$^{-1})$ peak divided by that of the 1030 cm^{-1} peak (SiOSi) for replicate preparation (procedure 1) and effect of aging. All peaks in the composite peak are indicative of methyl groups bonded to silicon (Si-CH$_3$).
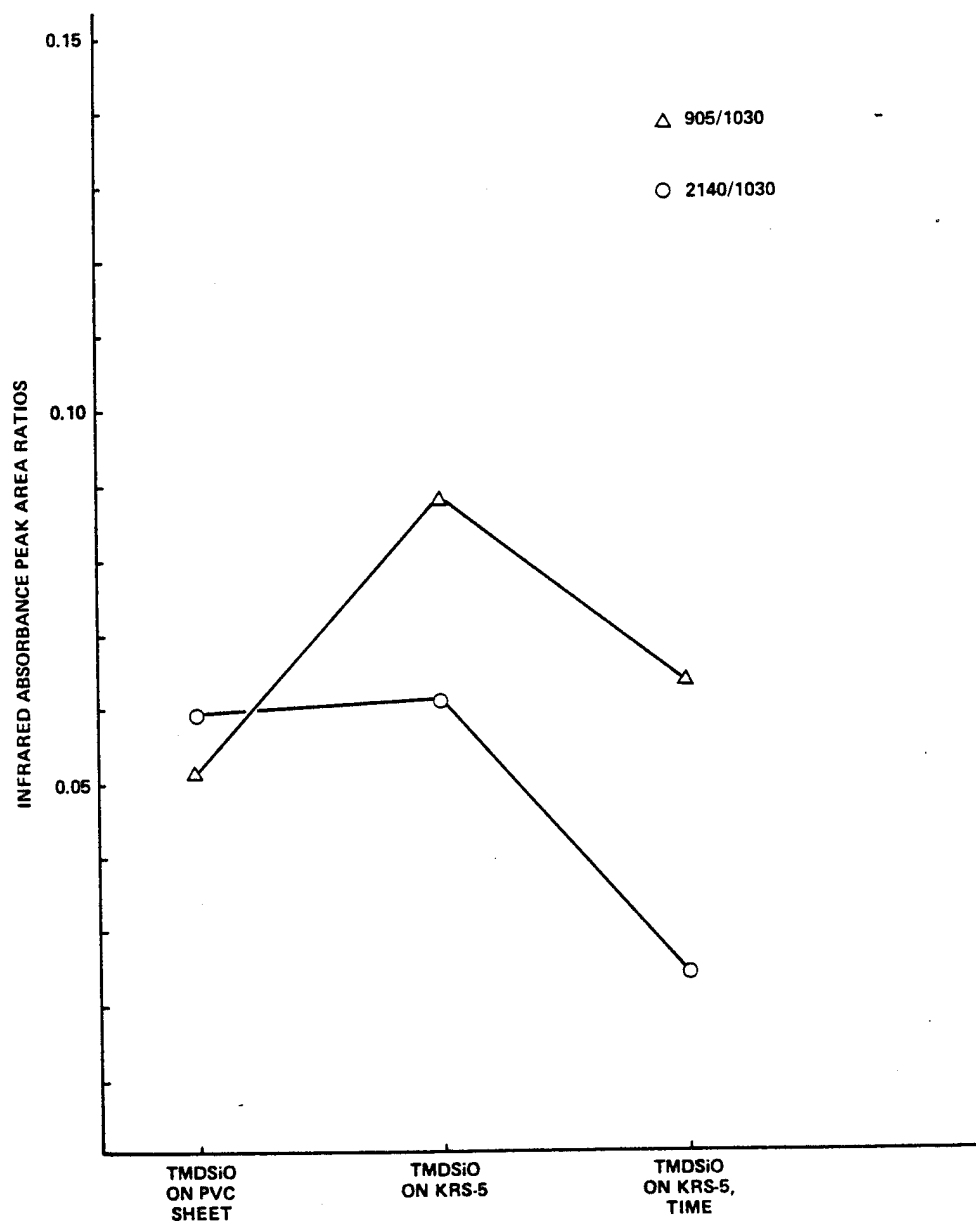
Figure 39. Infrared absorbance peak area ratios for replicate preparations of TMDSiO glow-discharge polymer by procedure 1 and effect of aging. The peaks are indicative of Si-H groups and peak areas are divided by that of the 1030 cm^{-1} peak (Si-O-Si).
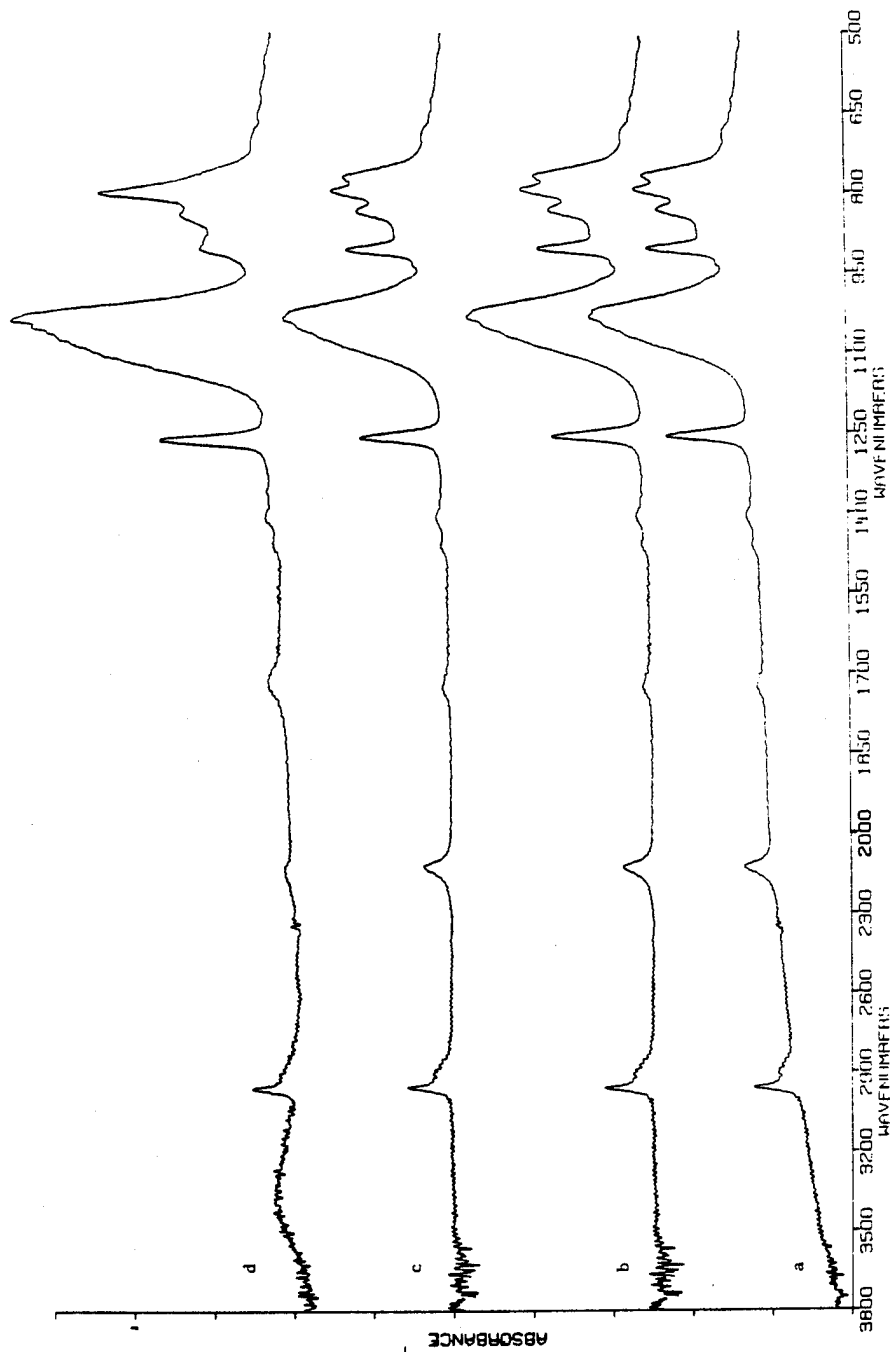
Figure 40. FTIR spectra of tetramethyldisiloxane glow-discharge polymer deposited on an internal reflection element by procedure 2 in Table V. The spectra were obtained at the following time intervals after deposition a.) 1 hr, b). 2 days, c.) 37 days, d.) 153 days.
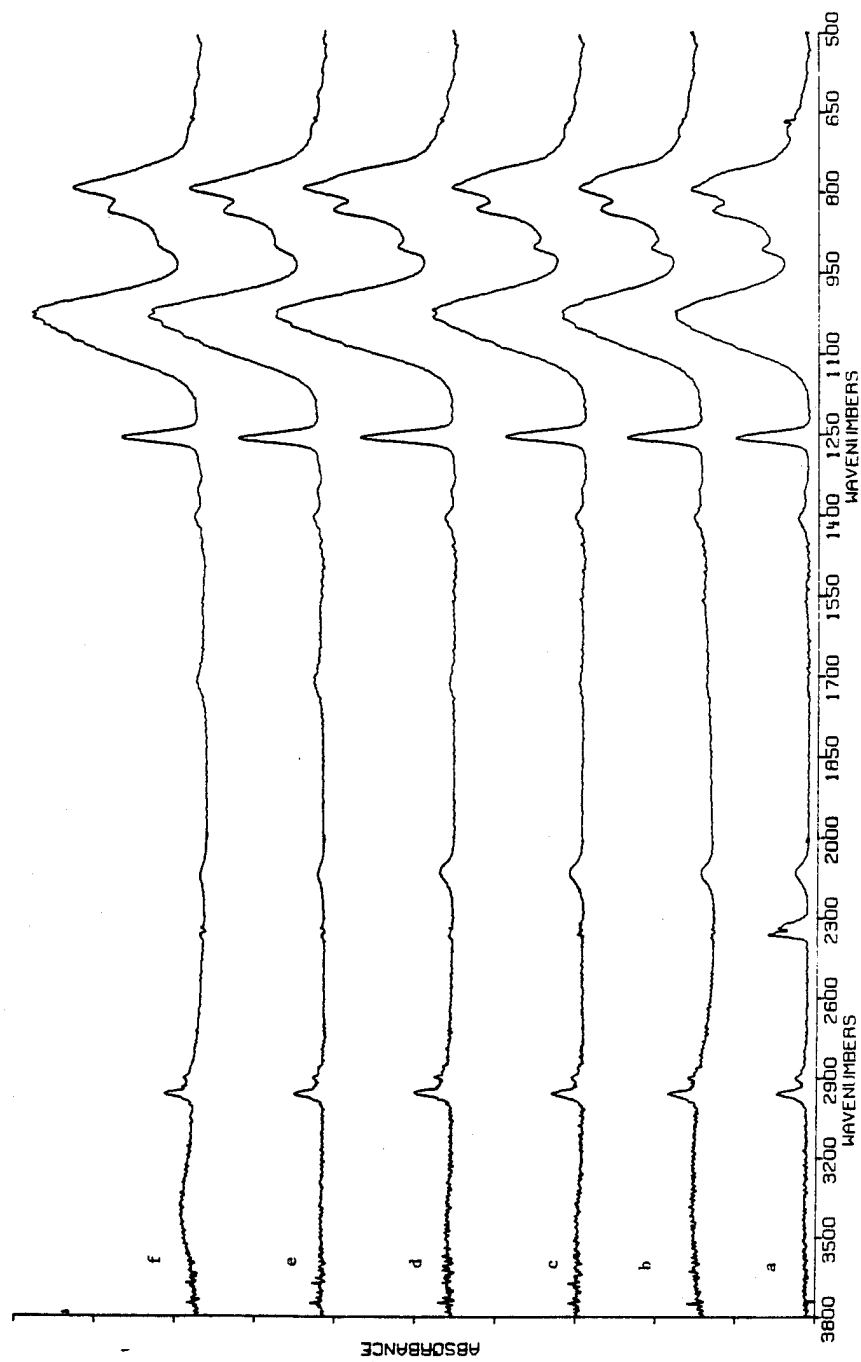
Figure 41. FTIR spectra of tetramethyldisiloxane glow discharge polymer deposited on an internal reflection element by procedure 1 in Table V. The spectra were obtained at the following time intervals after deposition a) 1 hr, b) 1 day, c) 3 days, d) 12 days, e) 91 days, f) 155 days. (Note peak at 2350 cm^{-1} is CO_2 in IR spectrometer.)

and a decrease in the Si-H peaks at 2140 and 950 cm^{-1}. The peak at 1700 cm^{-1} denotes a carbonyl group which is believed to form by reaction of oxygen with free radicals trapped in the glow discharge polymers. For procedure 2, the decrease of the Si-H peaks and of the 770 peaks is noted. Figures 34-39 tell the same story. A decrease in Si-H, Si(CH$_3$)$_3$, Si(CH$_3$), but a constant Si(CH$_3$)$_2$/Si-O-Si ratio is seen.

The broad peak at 3400 cm^{-1} may indicate the SiOH group. The Si-O-Si peak at 1030 cm^{-1} is observed to grow more and more asymmetric with aging. This may denote that longer Si-O-Si-O-Si runs are forming in the plasma polymer. Si-H groups may be converted to SiOH groups, which then react further to form Si-O-Si branches. Thus the polymer appears to be growing increasingly crosslinked with time.

2.2.1.2.3 FTIR Spectra of Tetramethyldisiloxane Glow Discharge Polymer Deposited by Moving Coil (Procedure 3)

Deposition of glow discharge polymer using a moving coil is appealing because there are, in principle, no limits to the length of tubing that can be coated in this manner. However, there are technical difficulties inherent in this procedure. One of these is that the chemical nature of glow discharge polymer varies with location. In general the chemical properties of the polymer will vary as a function of distance from the coil and on whether one is located upstream or downstream from the coil. The latter is reasonable for a narrow tube reactor because the most intense glow is located underneath the coil. Thus all atoms and ions located downstream from the coil have been subjected to this intense glow, whereas this is not the case upstream. In addition, the intense glow may generate some heat leading to changes in the morphology of the tube surface associated with an increase in temperature. In order to minimize both of these, the power to flow rate ratio was kept low when this procedure was used.

Tygon tubing was coated with TMDSiO glow discharge polymer by procedure 3. A piece of tubing was cut from the middle of the tubing and pressed against an IRE to obtain an FTIR spectrum. When the Tygon tube was removed, a layer of material adhered to the internal reflection element. A new spectrum was obtained of the adherent material. This

is compared to the spectrum for untreated Tygon tubing in Figure 42.
The spectrum for the adherent material is clearly a combination of the
spectra of DOP and TMDSiO glow discharge polymer. Every intense DOP
peak (as listed by Tabb and Koenig)[117] appears in the spectrum of
adherent material, either as a separate peak or as a shoulder. The PVC
peaks are completely absent, notably those at 1427 cm^{-1}, 690 cm^{-1} and
(640, 600 cm^{-1}). Thus the deposition of glow discharge polymer by this
method apparently causes DOP plasticizer to exude from the tubing and
to combine with glow discharge polymer at the surface.

The spectrum for TMDSiO glow discharge polymer (procedure 3) on
PVC tubing is also shown in Figure 42. It will be recalled that data
manipulation is required to obtain this spectrum free of PVC-DOP peaks.
It may be noted that there is an indication of peak shift at 1730 cm^{-1}
as noted by Tabb and Koenig for neat versus PVC plasticizing DOP. The
glow discharge polymer contains a higher proportion of Si-H bonds than
that produced by either of the other techniques.

Thus the procedure produced a polymer that is less fully reacted
than the other polymers without avoiding undesirable heating effects.
One way to avoid or minimize exudation of plasticizer is to crosslink
the surface of the Tygon tubing with an Argon glow discharge using a
stationary coil. This was carried out using a procedure outlined in
the description of leaching studies. Deposition of glow discharge
polymer by procedure 3 was then carried out and a ATR spectrum obtained.
No material adhered to the IRE and the spectrum in Figure 30 was obtained.

2.2.2 ESCA Investigations of Tetramethyldisiloxane Glow
       Discharge Polymer

Samples of tetramethyldisiloxane plasma polymer deposited by
procedure 2 (see Table V) were examined by means of ESCA to determine
the reproducibility of the procedure and to see the effect of aging on
the chemical nature of the surface. In order to guage the adhesion of
the glow discharge polymer to the Tygon tubing substrate, an ESCA
examination was made of the inside surface of Tygon tubing coated with
tetramethyldisiloxane glow discharge polymer and subsequently subjected
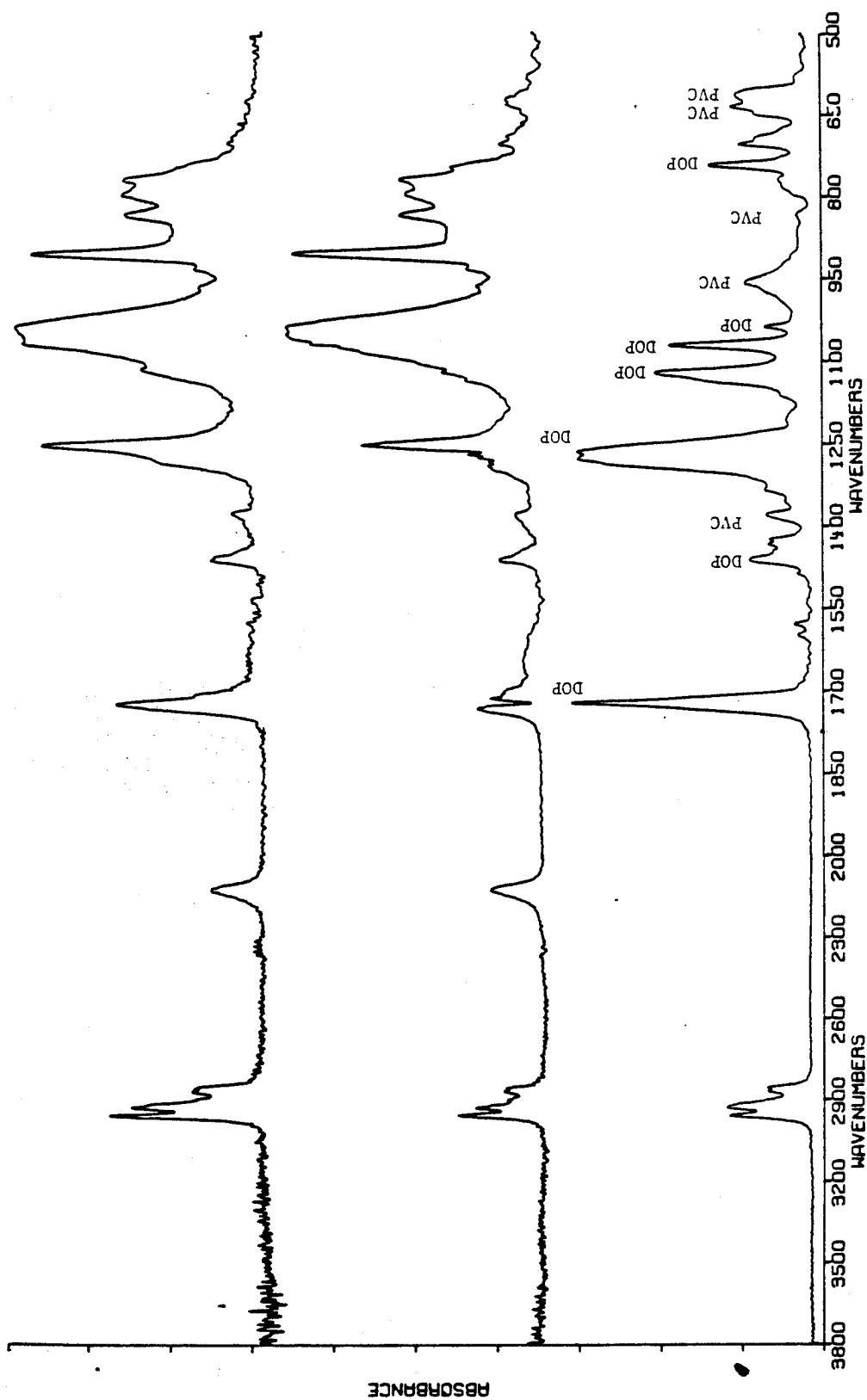
Figure 42. FTIR ATR spectra obtained for TMDSiO plasma polymer deposited inside PVC tubing with a moving coil (procedure 3 in Table V).

Top: Spectrum of layer adherent to IRE after pressing tubing against IRE, and then re-moving the tubing.

Middle: Spectrum obtained by ratio of single beam spectrum of plasma polymer on PVC tubing to single beam spectrum of PVC tubing.

Bottom: Spectrum of PVC tubing.

to a two hour flex test (see Section 2.2.3). The intensity of the spectral line for Cl was used as a gauge of the amount of PVC substrate uncovered during flexing.

The effect of aging on glow discharge polymer deposited on PVC sheet by procedure 1 was also followed by ESCA examination of one set of samples.

2.2.2.1 Experimental

TMDSiO glow discharge polymer was deposited on aluminum or PVC substrates. When the glow discharge polymer was deposited inside Tygon tubing, the tubing was slit open and cylindrical sections of the tubing were attached to ESCA strips with an instant adhesive, so as to present the inside surface of the tubing to the spectrometer. The sides of the cylindrical section were painted with carbon paint, thus assuring that any Cl detected in the spectrometer was from incomplete coverage of the inside surface.

PVC sheet specimens were cut into cylindrical sections prior to coating with TMDSiO glow discharge polymer by procedure 1 (Table V). In this way coverage of both sides and top surface of the cylinders with glow discharge polymer was assured. These cylinders were then attached to the ESCA stub with an "instant" adhesive.

ESCA spectra were obtained using a DuPont Model 650 spectrometer with a MgK_α x-ray source and equipped with a micro-computer data acquisition and processing system. The following spectral lines were obtained from each blank: C_{1s}, O_{1s}, $Si_{2p_{1/2}, 2p_{3/2}}$ and $(Al_{2p_{1/2}, 2p_{3/2}}$ or $Cl_{2p_{1/2}, 2p_{3/2}}$ depending on substrate).

2.2.2.2 Reproducibility of and Effect of Aging on Tetramethyldisiloxane Glow Discharge Polymer

ESCA spectra were obtained for glow discharge polymer deposited by means of procedure 2 inside Tygon PVC tubing. Two types of samples were examined. In one case a piece of aluminum foil, was placed at the center of a one foot long length of Tygon tubing. Two replicate preparations (procedure 2) were carried out in this fashion. Two additional preparations were carried out with no aluminum foil and the inside of the tubing was examined by ESCA as described in the preceding section.

As it is possible (but not probable) that changes in TMDSiO glow discharge composition detectable by ESCA could be found along the length of the aluminum strip or near the center of the tubing, an effort was made to avoid an upstream or downstream geometrical sequence in choosing samples for the time sequence.

The results are shown as elemental ratios in Tables IX and X. There is a clear increase in oxygen relative to carbon and silicon as a function of time. However the C/Si ratio remains constant. The mean C/Si ratio and standard deviation are given at the bottom of each C/Si column in Tables IX and X. The standard deviation is never greater than 7%. For the 19 (replicate preparation) - time combinations in the two tables the C/Si ratio is 2.49 with a standard deviation of 8%.

The increase of the O/Si ratio with time is shown in Figure 43 in a semi-log plot, the same is done for the O/C ratio in Figure 44. The increase in oxygen may be caused both by reaction of oxygen with free radicals in the glow discharge polymer and with Si-H groups. For the longest times (170-225 days) only data for glow discharge polymer on aluminum is available. ESCA spectra were obtained for the glow discharge polymer on Tygon tubing (after 170-225 days) but is not included in the figures or tables because a $Cl_{2p_{3/2}, 2p_{1/2}}$ peak was detected indicating that PVC is being seen by the spectrometer.

An indication of the reproducibility of the preparation of the glow discharge polymerization procedure is given by the elemental ratios for the four replicate preparations at the shortest times after preparation of the samples (1-2 hours). These are: C/Si = 2.56 ± 3%, O/Si = 0.86 ± 7%, O/C = 0.34 ± 8%. It may be noted that figures 43 and 44 tend to exaggerate the variation between samples, as in both cases the ordinate axis does not start at zero.

A ESCA study of the effect of aging on tetramethyldisiloxane glow discharge polymer deposited on PVC sheet by procedure 1 (Table V) was also carried out. No systematic change in O/Si or O/C ratio was observed for 2 hours to 114 days aging. However a Cl peak was detected for all but the 2 hour sample and this experiment should be repeated. The elemental ratios for the 2 hour sample and the mean elemental ratio for four samples (aging = 2 hours, 15 days, 26 days, and 114 days) are given in Table XI.

Table IX

ESCA Elemental Ratios for TMDSiO Deposited by

Procedure 2 on Al

Aging Time (days)	Sample 1			Sample 2		
	C/Si	O/Si	O/C	C/Si	O/Si	O/C
0.06	2.50	0.79	0.32			
0.08				2.50	0.93	0.38
1	2.45	0.86	0.35	2.44	0.95	0.39
3				2.10	1.04	0.50
6	2.50	1.005	0.40			
7				2.29	0.95	0.41
17				2.37	1.12	0.48
19	2.71	1.019	0.38			
175				2.10	1.26	0.60
207	2.41	1.340	0.56			
Mean	2.51 ± 0.12			2.3 ± 0.17		

Table X

ESCA Elemental Ratios for TMDSiO Deposited by

Procedure 2 on Tygon Tubing

Aging Time (days)	Sample 1			Sample 2		
	C/Si	O/Si	O/C	C/Si	O/Si	O/C
0.042	2.58	0.83	0.32	2.65	0.89	0.334
1	2.40	0.79	0.33	2.5	0.89	0.357
6	2.62	0.92	0.35			
7				2.61	0.94	0.361
20	2.61	0.96	0.37			
21				2.94	1.082	0.368
Mean	2.55 ± 0.10			2.68 ± 0.18		

Table XI

Elemental Ratios by ESCA for TMDSiO Glow-Discharge Polymer Deposited

by Procedure 1 on PVC Sheet

Sample Designation	C/Si	O/Si	O/C
2 hours after deposition	2.51	1.02	0.41
Mean for four samples	2.63 $\pm$ .23	0.96 $\pm$ .08	0.37 $\pm$ 0.028
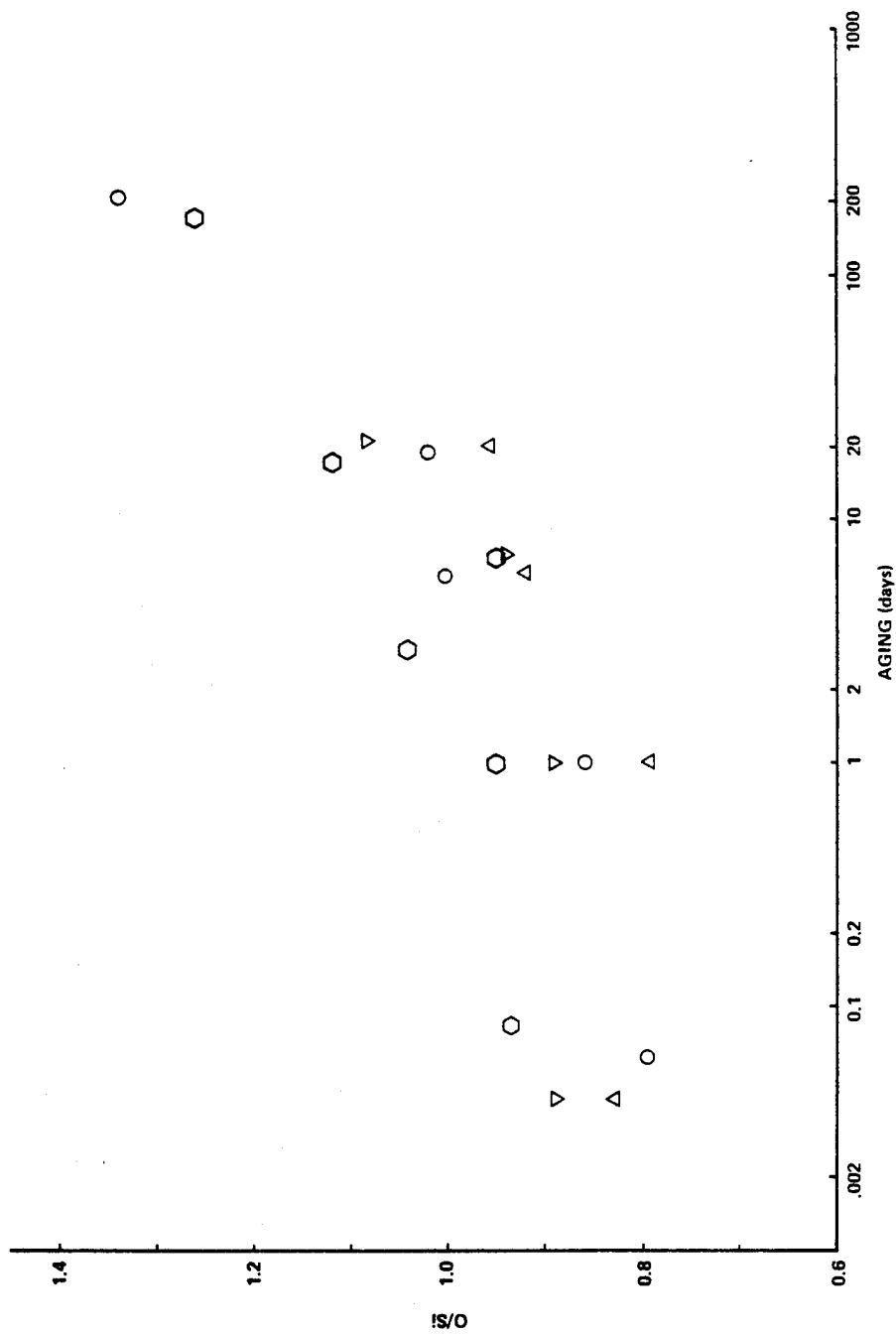
Figure 43. O/Si ratio (from ESCA data) plotted vs log time for TMDSiO glow-discharge polymer deposited by procedure 2. Triangles refer to glow discharge polymer on PVC tubing; other symbols to glow discharge polymer on aluminum foil.
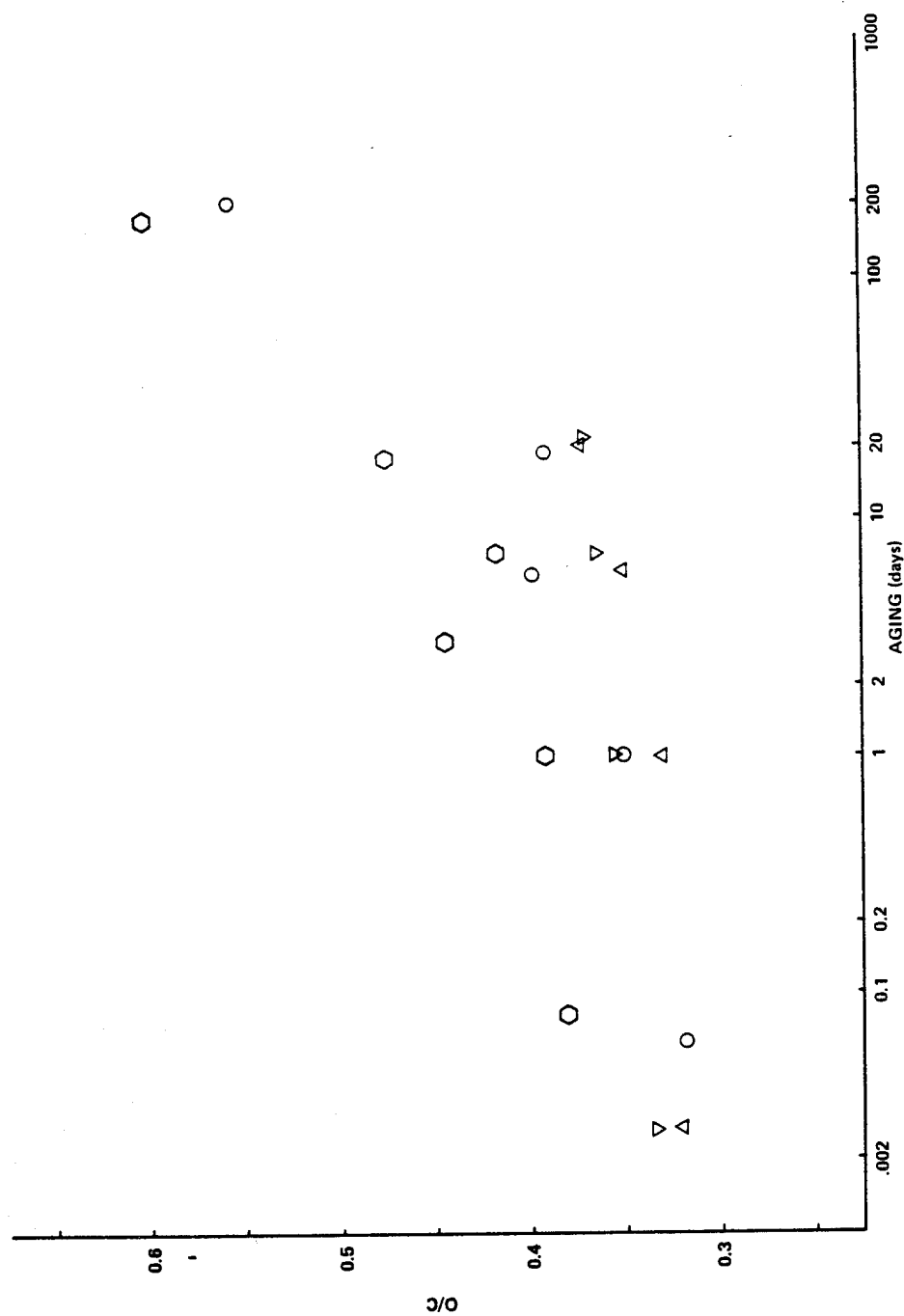
Figure 44. O/C ratio (from ESCA data) plotted vs log time for TMDSiO glow-discharge polymer deposited by procedure 2. Triangles refer to glow discharge polymer on PVC tubing; other symbols to glow discharge polymer on aluminum foil.

2.2.2.3 Adhesion of Tetramethyldisiloxane Glow Discharge Polymer
to Tygon Tubing

An ESCA analysis of the inside surface of Tygon tubing, coated with
1000 $\overset{o}{A}$ of TMDSiO glow discharge polymer, was carried out after a 2 hour
flex test (15,600 flexes) in a peristaltic pump according to the procedure
described in Section 2.2.3.1. The following spectral lines were monitored:
C_{1s}, O_{1s}, $Si_{2p_{3/2},2p_{1/2}}$, and $Cl_{2p_{3/2},2p_{1/2}}$. Detection of a Cl line
would indicate imperfect adherence of the glow discharge polymer coating.

Samples were taken from three sites on the inside of the tubing
from the middle of the foot long length of tubing. These sites were the
outside, edge and inside of the tubing. These designations are fully
explained in Section 2.2.3. The inside is the part crushed by the
roller of the peristaltic pump, the edge is the part where maximum
flexing occurs and the outside is the part that lies on the track. The
tubing was washed with distilled, deionized water immediately following
the flex test and then cut and mounted on the ESCA stubs.

The signals (corrected for photoelectron cross section) observed
for each element, and elemental ratios are given in Table XII. No
chlorine signal is seen except for the "edge" sample. In the latter
case, the signal is barely perceptible over the noise. Thus even for
the edge, which undergoes maximum flexing, almost complete coverage is
maintained. Coverage is complete for the outside and inside samples.
The elemental ratios are completely different from that observed for
freshly-coated (non-flexed) tubing indicating the presence of plasticizer
or detergent at the surface.

2.2.3 Creation of a Barrier to Leaching of Plasticizer From
Poly(vinyl chloride) Tubing By Glow Discharge Treatment
or Glow Discharge Polymer Coating

The current interest in leaching of plasticizer from poly(vinyl
chloride) polymers stems, at least in part, from the disclosure in 1970
and thereafter that plasticizer is extracted by blood from poly(vinyl-
chloride) blood bags and tubing.[118-122] In some of these papers atten-
tion is drawn to the fact that the plasticizer, commonly referred to as

Table XII

ESCA Elemental Ratios for TMDSiO Glow-Discharge

Polymer Coated Tygon Tubing after Flex Test

Sample Designation	C/Si	O/Si	O/C
Outside	8.4	2.12	0.252
Edge	3.62	1.21	0.334
Inside	4.16	1.24	0.298

dioctylphthalate (DOP), is actually di(2 ethylhexylphthalate). We make note of this fact and continue to refer to the leached plasticizer as dioctylphthalate (DOP).

For poly(vinylchloride) tubing in a hemodialysis unit, Jaeger and Rubin found that 15 mg/l of plasticizer was extracted in 8 hours when using blood. However, no extraction could be detected when saline was used over a 5 hour time period.[118,123] It was suggested that lipoproteins in the blood solubilize the plasticizer thus lifting it off the inside surface of the tubing to which additional plasticizer may then migrate. To approximate the solubilizing action of blood, we have used an 0.5% solution of sodium lauryl sulfate either in a static mode in a one foot coil of PVC tubing or flowing through the tubing as it is alternately compressed and released in a peristaltic pump. The concentration of detergent may be compared with the concentration of total serum lipid: 400-1800 mg/100 ml.[124]

The inside of one foot lengths of tubing were treated with argon plasma or coated with tetramethyldisiloxane plasma polymer in order to form a barrier that would inhibit the leaching of DOP from PVC. After exposing the inside of the tubing to 0.5% sodium lauryl sulfate solution, the solution was assayed for the presence of DOP by means of ultraviolet absorption spectrometry.

2.2.3.1 Experimental

2.2.3.1.1 Glow Discharge Treatment and Glow Discharge Poly merization

Poly(vinylchloride) tubing was glow discharge treated or coated in the apparatus shown in Figure 45. A one-foot long coil of Tygon R3603 tubing was placed in the middle of the straight tube reactor. The tubing chosen was found to yield relatively reproducible rates of DOP leaching in a peristaltic pump using 0.5% detergent solution. Less well-known brands of tubing were found to occasionally exude relatively massive amounts of material from the zone of maximum flexing (edge) yielding a suspension of particles that visibly scatter light.

The reactor shown in Figure 45 can be used in two ways. In one the coil is held stationary in the position shown in the figure. As there is a tendency for the deposition rate to be greater near the coil and less further away (see the last annual report), the stopcocks can be
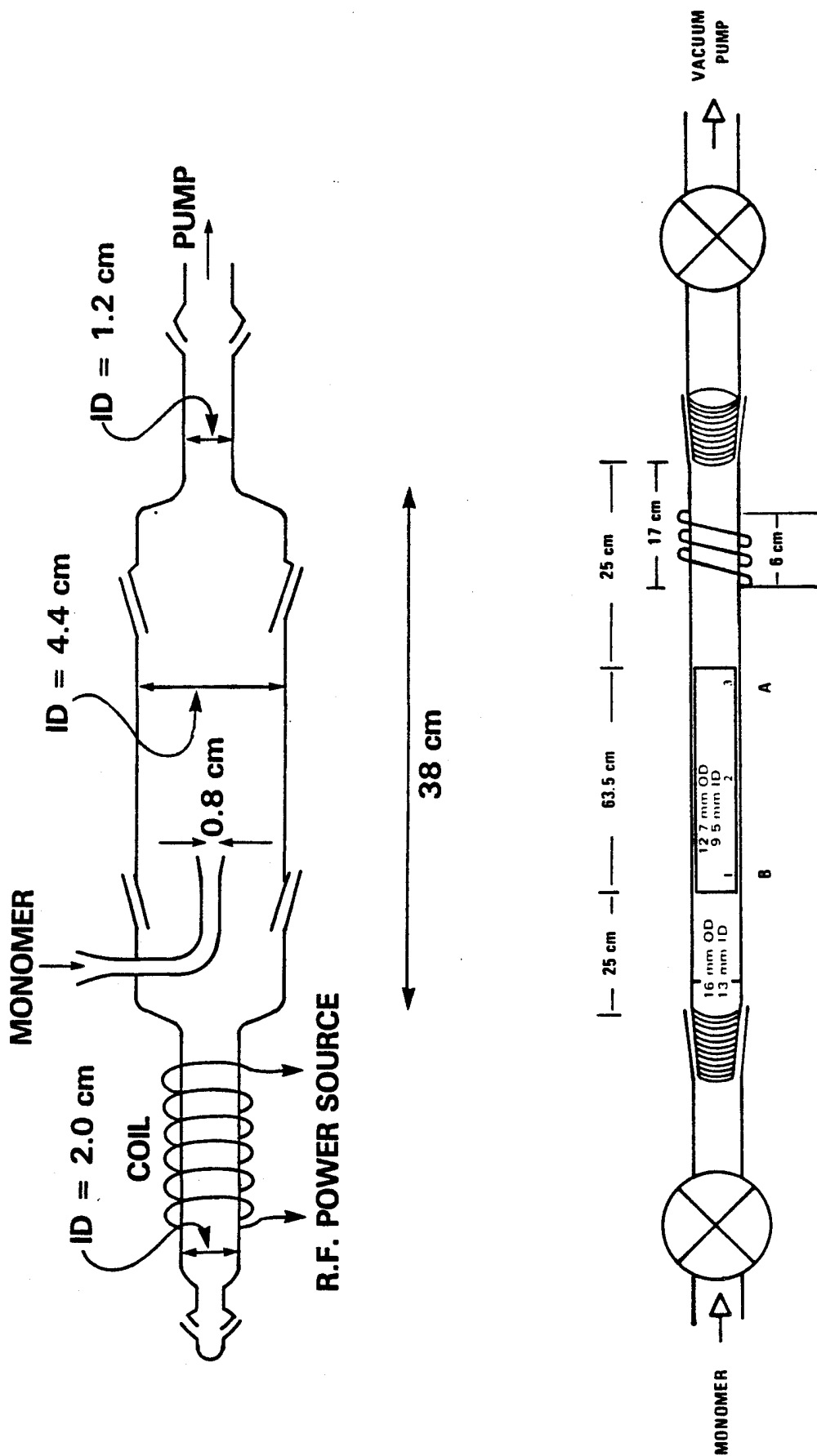
Figure 45. Schematic representations of standard reactor (top) and straight tube reactor (bottom). The straight tube reactor is used for glow discharge treating or coating of PVC tubing.

closed half-way through the coating (or glow discharge treatment) and the orientation of the reactor reversed (with regard to the monomer flow) so that end B of the Tygon tubing (formerly furthest from the coil) becomes the end closest to the rf coil which activates the glow discharge. The stopcocks are then opened and coating (or treatment) resumed. Thus a more even glow discharge polymer or glow discharge treatment is effected. Alternatively, the coil can be moved over the tube as the glow discharge polymer coating or glow discharge treatment is applied. As the power density of glow discharge under the coil is considerably higher than that elsewhere, the latter procedure subjects the Tygon tubing to a range of power densities. Because of the high power density directly under the coil, the chemical nature of glow discharge polymer deposited upstream from the coil is generally very different (for TMDSiO, more silicon rich) from that deposited downstream from the coil. Thus for glow discharge polymerization, the glow discharge polymer deposited by the moving coil method is far from uniform. Thus although the moving coil method is appealing for its potential as a means of coating very long pieces of tubing, the stationary coil method was most extensively used because of the uniformity of the glow discharge polymer or treatment.

A Tegal 300W RF generator supplied power to the glow discharge and was run either in a continuous mode or in the pulsed power mode. For the latter case, nominal times on and off were 3.3 and 33 milliseconds, respectively; the actual times were found to be 0.4 and 2.65 milliseconds, respectively.

2.2.3.1.2 Assay for Dioctyl Phthalate by Ultraviolet Absorption Spectrometry

DOP yields an ultraviolet absorption spectrum of the type shown in Figure 46a. The 0.5% sodium lauryl sulfate solution run through the 2 hour peristaltic pump flex test yields the UV spectrum given in Figure 46b. Both show peaks (or plateaus) at 225 nm and at 275 nm. The height of these two peaks was used as an assay for the presence of DOP in 0.5% detergent solution that had contacted surface modified or untreated Tygon tubing.
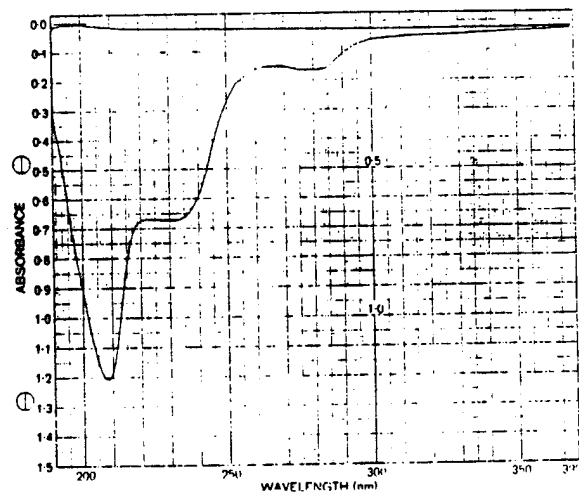
(a)
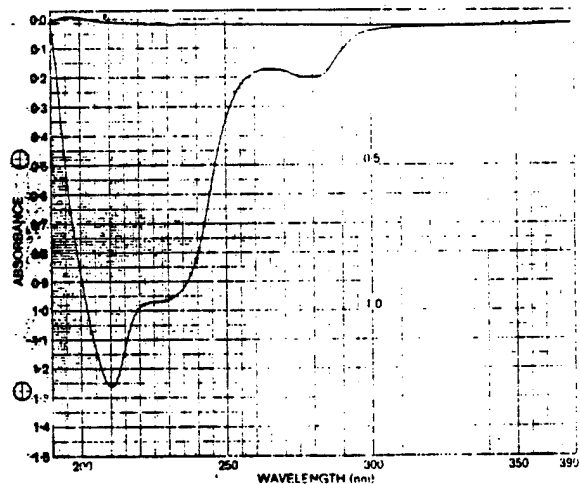
(b)

Figure 46. Ultraviolet absorption spectrum for dioctyl phthalate solution
            in 0.5% sodium lauryl sulfate (top) and for flex test solution
            using uncoated PVC tubing (bottom). Spectra are run with 0.5%
            sodium lauryl sulfate in reference cell.

UV absorption spectra were obtained on a Perkin Elmer model 402 ultraviolet/visible spectrophotometer using 1 cm path length quartz cells. In addition a Gibson model 260 double beam UV monitor was used to continuously measure the UV absorption at 254 nm during the course of the flex test.

The calibration of the UV absorption was made by dissolving known volumes of DOP in ethanol and then adding the ethanol solution to a sodium lauryl sulfate solution so as to effect a 1% ethanol, 0.5% sodium lauryl sulfate solution containing a known concentration of DOP. The use of an ethanol solution intermediate insured dispersal and solution of DOP in the calibration solutions. The calibration graph obtained is shown in Figure 47.

2.2.3.1.3 No-Flow and Flex Tests of Tygon Tubing

Two modes of effecting contact of 0. 5% detergent solution with Tygon tube surface were used. In one (No-Flow) a 2 inch long piece of glass tubing (O.D. = 3/8") was inserted into one end of the one foot length of Tygon tubing, the assembly was filled with 0.5% sodium lauryl sulfate solution, and a closed loop formed by connecting the two open ends. The assembly was allowed to lie on a laboratory table for four hours before removal of the solution for subsequent measurements of UV absorption.

In the flex test a one foot length of 3/8" I.D. Tygon R3603 tubing was placed in a peristalitic pump (Manostat Varistaltic, Cat No. 72-895-05-00) whose track was lined with Teflon film, with the rotor running in a clockwise fashion at 60 revolutions per minute. This caused 120 compressions of the tubing per minute (rollers on each of the two ends of rotor) with rollers traveling upward along the track whose plane was inclined at an angle of approximately 48° with respect to the horizontal. The rest of the loop was completed as shown in Figure 48 by a glass loop with two arms leading to the Gibson Model 260 double beam UV monitor (254 nm). Teflon tubing (I.D. = 3 mm) led to and from the UV monitor. A 2 1/4" long piece of 1.5 mm I.D. glass capillary was included in the loop to induce a portion of the detergent solution to flow through the UV monitor. This is obviously a very demanding test for any barrier to leaching involving flexing and expansion of the tubing as well as rapid flow of the soap solution past the inside surface. However, the design
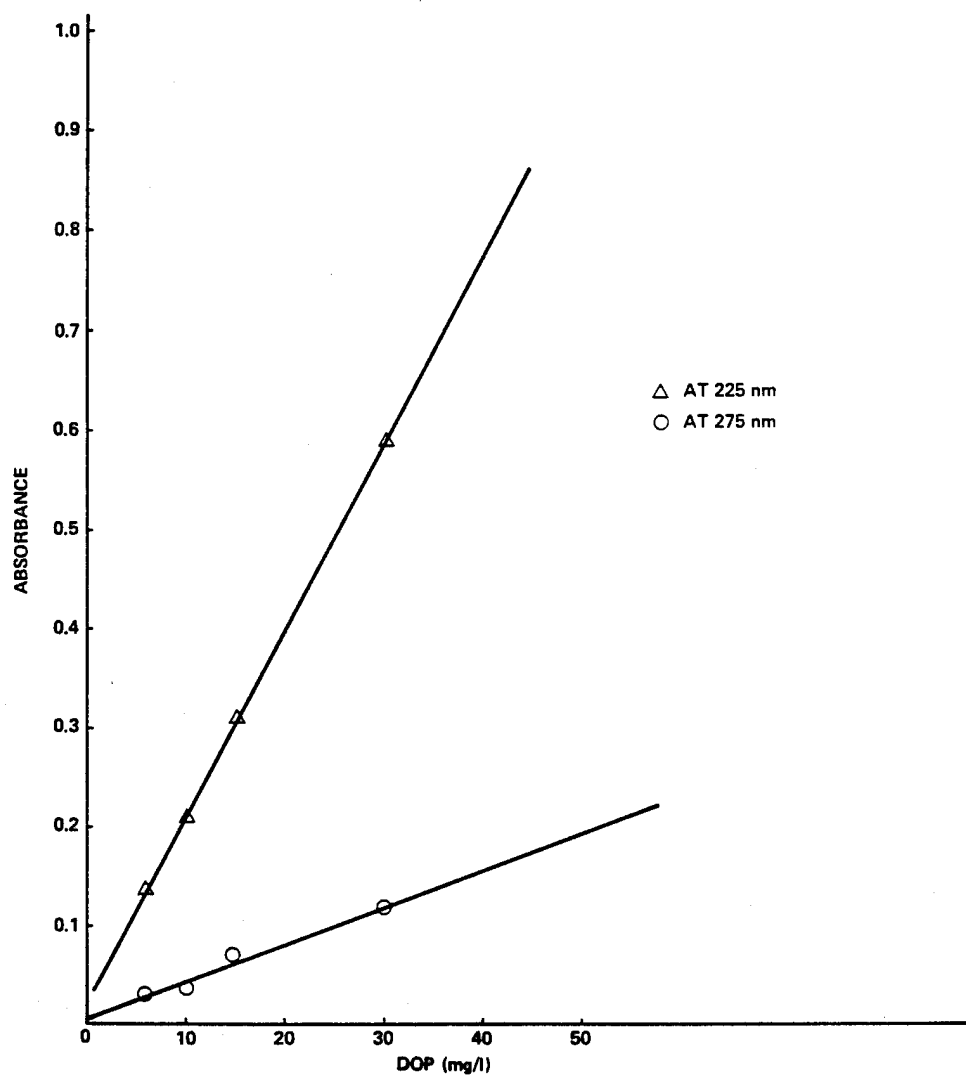
Figure 47. Ultraviolet absorbance calibration graph for dioctylphthalate.
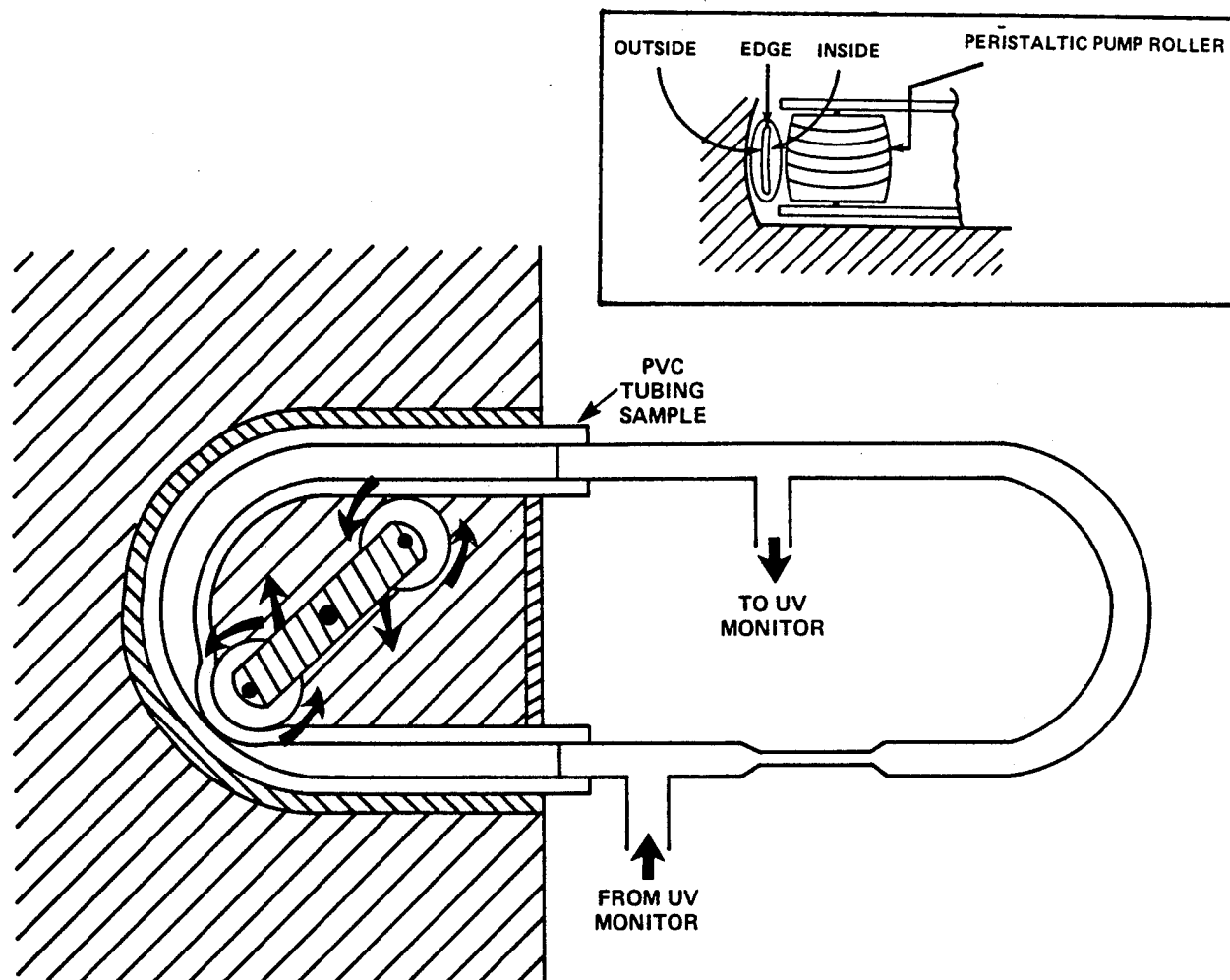
Figure 48. Schematic representative of flex-test using peristaltic pump.

of the peristaltic pump is such that only half of the one foot length that fits into the pump is exposed to the pump rollers. A two hour flex test (15,600 flexes) was normally run.

2.2.3.2 Results

2.2.3.2.1 Argon Glow Discharge Treatment of Tygon Tubing

Argon plasma treatment of Tygon tubing was found to be the most effective in reducing the leach rate of DOP plasticizer. The tube was subjected to a 2 hour flex test as described earlier and contained 35 ml of 0.5% sodium lauryl sulfate. When the flex test was run on untreated tubing, a concentration of at least 23.5 mg/l of DOP was detected by UV, amounting to a total mass of 0.82 mg of DOP leached from the tubing. The ultraviolet monitor showed the leach rate to be constant; the amount of DOP in the solution increased linearly with time. This linear increase was also observed for all argon plasma treated tubes. The reduction of leach rate by means of argon plasma treatment is shown in Figure 49 and is expressed as % of the leach rate for untreated tubing. This was obtained by dividing the concentration of DOP after a 2 hour flex test (as obtained by UV) by the 23.5 mg/l obtained for uncoated Tygon tubing. The conditions of argon plasma treatment are: a stationary coil, a flow rate of 0.08 cm^3/min, P_o = 12 millitorr and power of 35 or 50 Watts with a corresponding P_g of 26 and 32 millitorr respectively. The treatment decreases the leach rate to as little as 30% of the leach rate from untreated tubing. As would be expected, operating at higher power results in a low leach rate after shorter treatment times. A limit to the inhibition of leaching is approached asymptotically. For a 6 minute treatment at 50W three replicate treatments of tubing were made and good agreement in the diminution of leach rate was obtained. One of these replicate treatments was made immediately after washing the tubing and one 2.5 days after washing. It appears that any migration of plasticizer to the tube surface over a 2.5 day period after washing does not affect the end result. Replicate treatments were carried out at 35 watts for 12 minutes, as well. Here the open squares represent the results for one consecutive set of preparations. The filled in squares represent replicate treatments carried out subsequently. Diminution of leach rate varies from 31% to 48%.
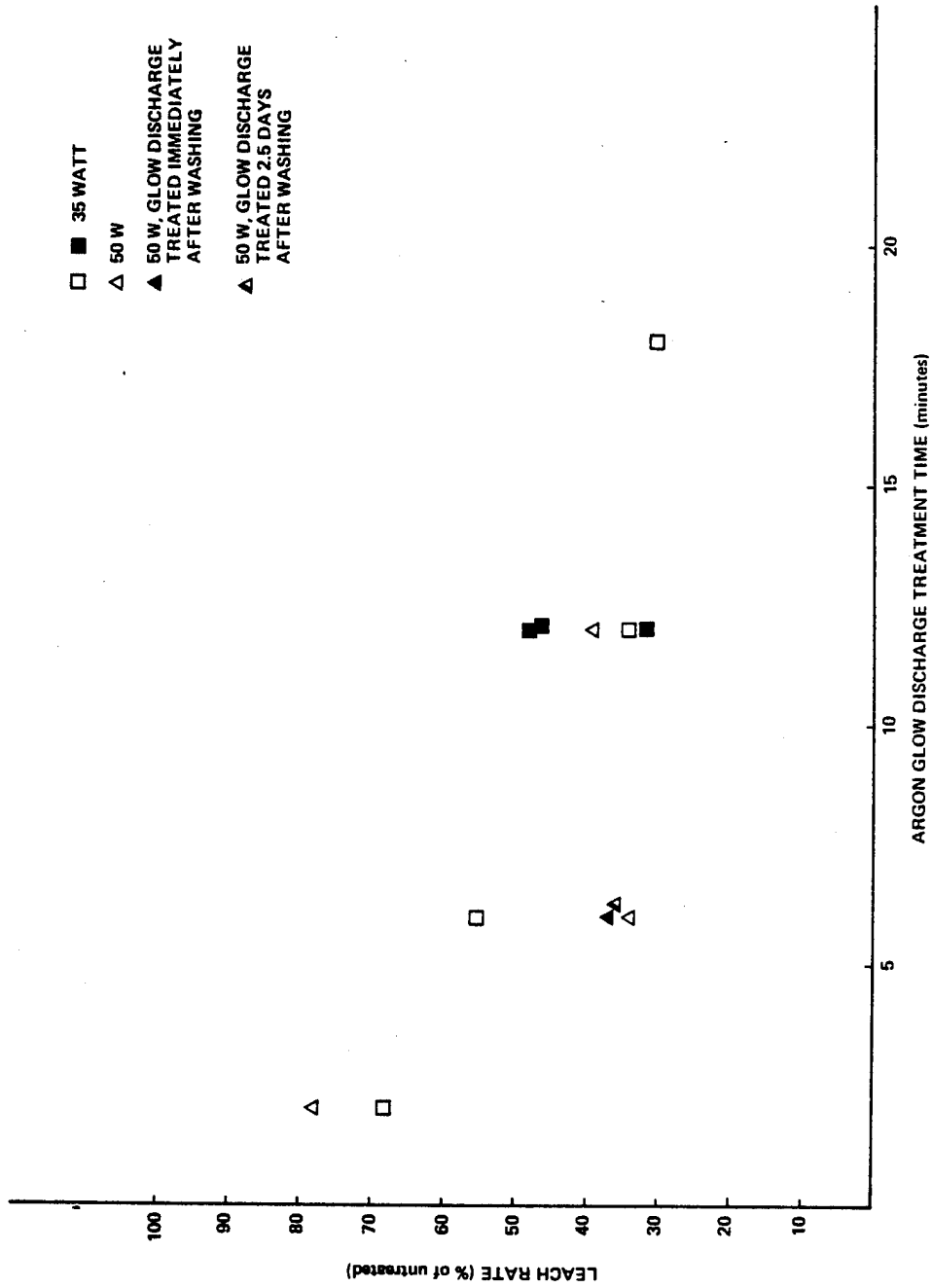
Figure 49. Leach rate (% of that for untreated tubing) as a function of Argon glow discharge treatment time using a 2 hour flex test.

It may be noted that a diminution of the leach rate to 30% of untreated tubing is quite respectable for this rather demanding flex test. A greater effect would be expected for the no-flow 4 hour test, which is detailed in Section 2.2.3.2.2. Diminution of the DOP concentration to as low as 4% of that for no treatment was observed for PVC tubing treated with Argon plasma for 12 minutes at 35 Watts in a 4 hour no-flow test.

Argon plasma treatment at lower powers: 20 Watts, 35 Watts pulsed and 50 Watts pulsed did not result in the dramatic drop in leach rate in the flex test that had been observed for the 35 Watt and 50 Watt treatments. Treatment times up to 36 minutes were used for these lower powers. However a drop to 50% of the untreated tubing leach rate in the flex test was observed using a moving coil for a 35 Watt argon glow discharge with a total treatment of 2 minutes. No systematic study of this mode of glow discharge treatment was carried out, however.

The diminution of leach rate is caused by the creation of a cross-linked polymer skin on the surface of the Tygon tubing. This was demonstrated by dissolving pieces of untreated and Argon glow discharge treated tubing (35 Watts, 18 minutes) in tetrahydrofuran (THF). After 24 hours the untreated tubing was completely dissolved. A non-dissolving skin was noted at the inner surface of the argon glow discharge treated tubing after the first hours in the THF. This skin did not dissolve after a week in THF.

The effect of argon glow discharge treatment on the morphology of PVC tubing can be seen in scanning electron micrographs of treated and untreated tubing after the two hour flex test (see Figure 50). The untreated tubing shows no cracks and a well defined region of debris at the flex line on the edge. The argon glow discharge treated tubing shows cracks on the inside surface and the edge. The concentration of cracks is much less on the outside where less flexing occurs. The concentration of cracks is greatest on the edge and the flex line is noted not by the accumulation of debris but by the large concentration of cracks. The cracks are all less than a micron in width, and therefore are of a dimension that can be "tolerated" by blood in contact with the surface due to the adsorption and geometrical leveling provided by the earliest deposited biological layer.[125]
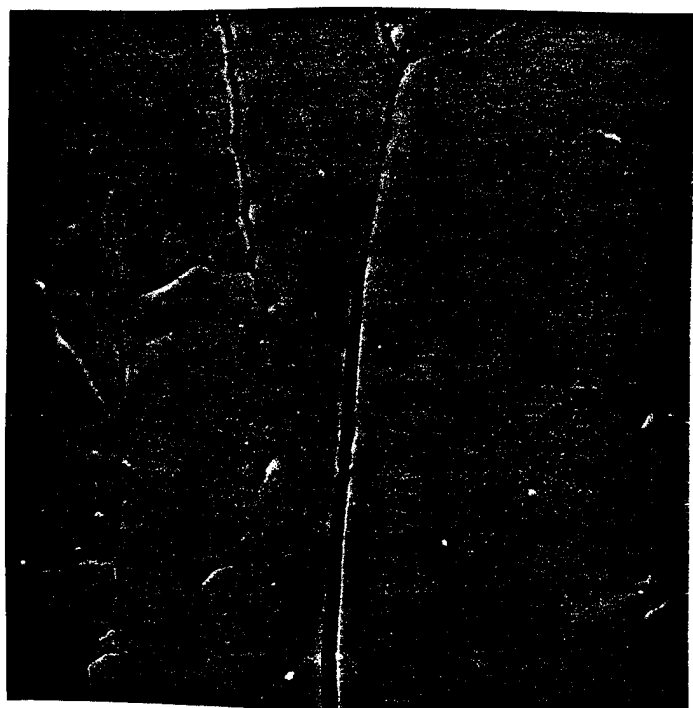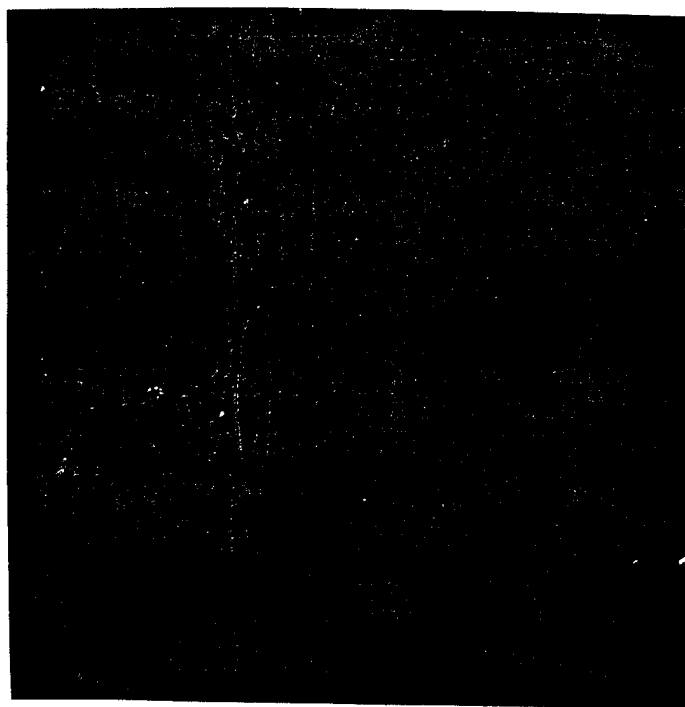
Figure 50a.   Scanning electron micrographs of argon glow discharge treated
              Tygon tubing after 2 hour flex test. Micrographs are of flex
              line on the edge of the tubing.
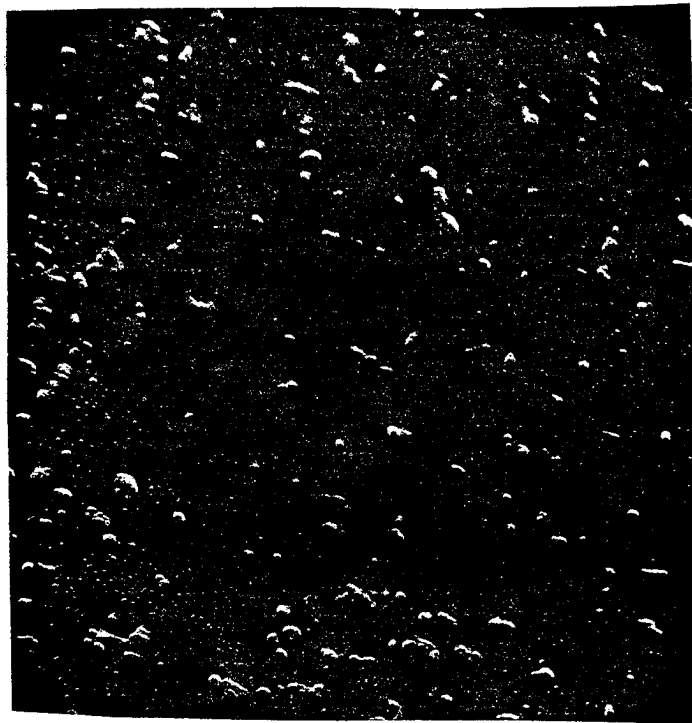
├───────┤ 10 μm
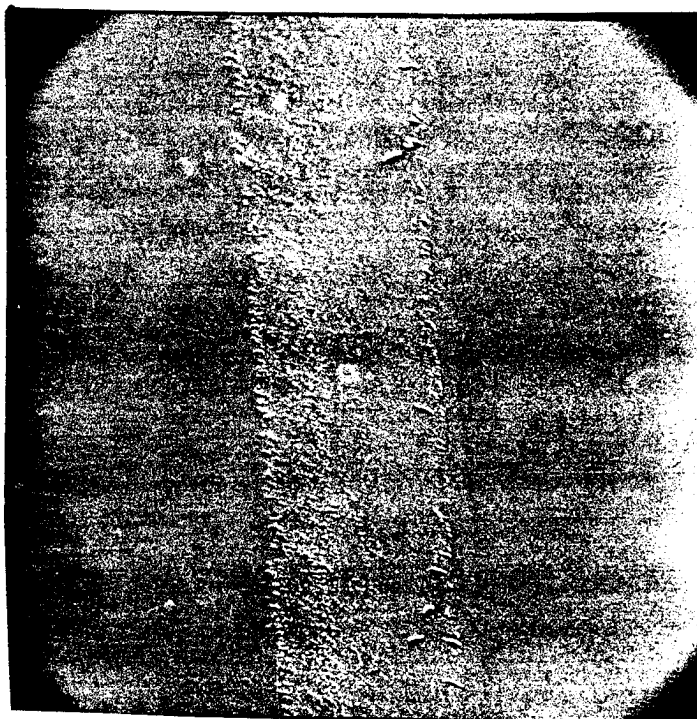
├───────┤ 100 μm

Figure 50b. Scanning electron micrographs of untreated Tygon tubing after
            2 hour flex test. Tubing is from same coil as used for samples
            yielding 50a. Micrographs are of flex line on the edge of
            the tubing.

2.2.3.2.2 <u>Coating with Tetramethyldisiloxane Glow Discharge Polymer</u>

As no conditions could be identified for which the deposition of a glow discharge polymer of tetramethyldisiloxane would result in an appreciable diminution of leach rate for DOP using the 2 hour flex test, a less extreme and more rapid test of leach rate was sought. The purpose of this test was to identify the best conditions for forming a TMDSiO glow discharge polymer barrier to leaching of DOP. It was found that an appreciable rate of leaching could be obtained by simply allowing 0.5% sodium lauryl sulfate solution to be contained, without agitation, in a closed loop of Tygon R3603 tubing. For untreated Tygon tubing the mass of DOP leached into 0.5% sodium lauryl sulfate solution was obtained as a function of time. For the first four hours the leach rate appeared to be constant. For this reason a no-flow test in which the detergent solution rests in the tubing for 4 hours was chosen to gauge the effect of glow discharge polymer coating on leach rate. Although each tube is in contact with the detergent solution for more time in the no-flow test than in the flex test, there are no equipment requirements in the no-flow test and a large number of tubes can be tested simultaneously.

Tetramethyldisiloxane glow discharge polymer was deposited inside Tygon tubing using procedure 2 in Table V. The conditions were monomer flow rate = 0.46 cm^3/min, P_g = pressure in glow discharge = 30 millitorr, power = 60 Watts pulsed. A reduction of leach rate to approximately 30% of that observed with no coating is observed for a 6,000 Angstrom thick coating (see Figure 51). The diminution is less for thinner and thicker coatings. The lesser leach rate for thicker coatings is probably caused by the delamination that is observed for thick coatings of glow discharge polymer. The indication that there is an optimum thickness of glow discharge polymer for the observed decrease in DOP leaching suggests that the leaching is inhibited by the glow discharge polymer rather than by any modification of surface of the Tygon tubing by the glow discharge. It may be noted that although the pressures are similar in the glow discharge coating and treatment procedure, the power used is much greater for efficacious argon glow discharge treatment. Also EPR experiments carried out in the early years of the contract suggested that ultraviolet radiation was able to impinge on the surface only in the early stages of
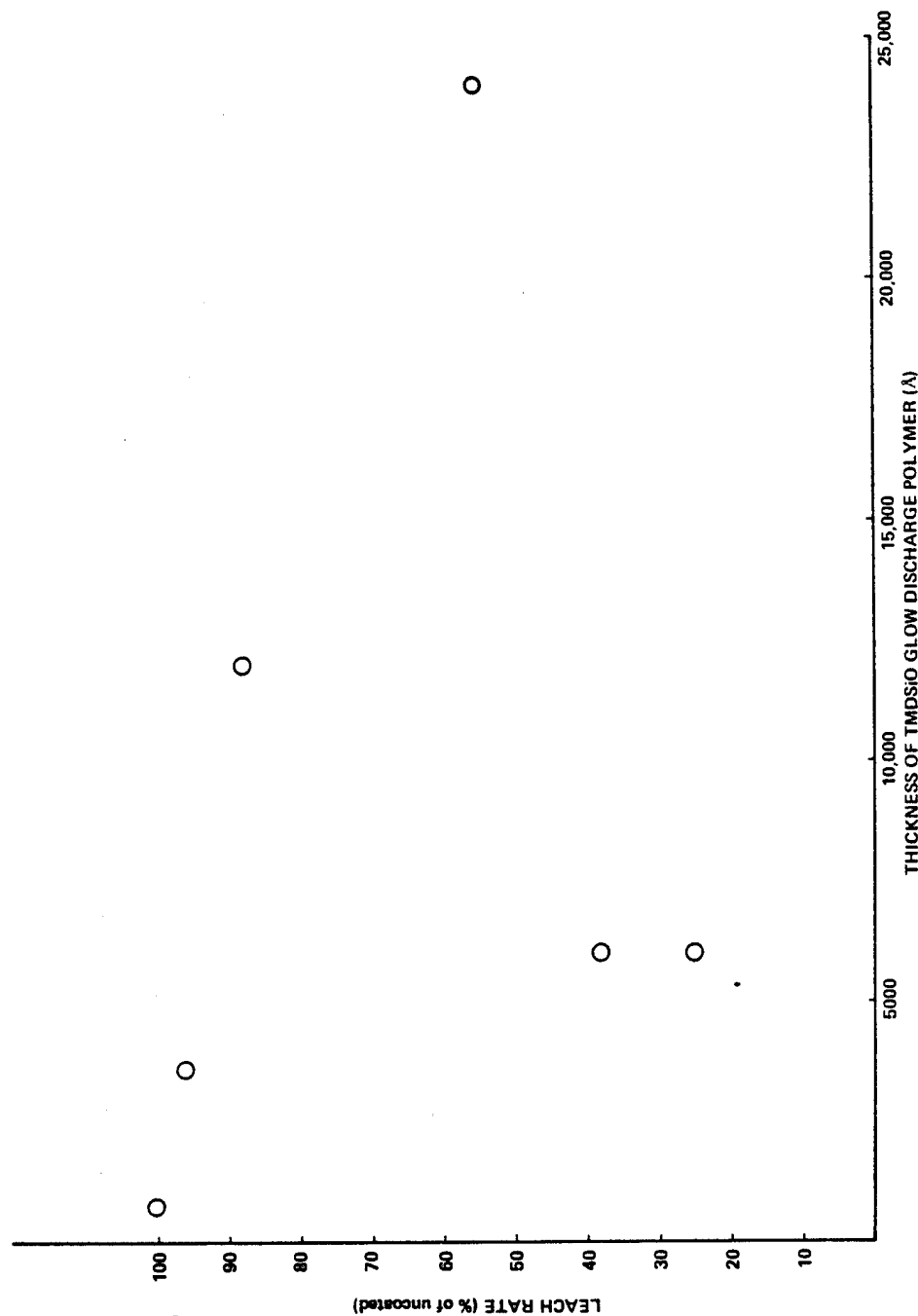
Figure 51. Leach rate (% of that for untreated tubing) as a function of thickness of TMDSiO glow-discharge polymer coating using 4 hour no flow test. Glow discharge polymer was deposited using procedure 2.

the coating procedure.[126] In later stages the coating acted as a barrier to the penetration of UV. The same is obvious for the less penetrating ions and electrons in the glow discharge.

The tube that yielded the 25% leach rate in Figure 51 (6000 $\overset{o}{A}$ of TMDSiO) was subjected to a second no-flow test 3 weeks later after first being cleaned by holding an 0.5% Na lauryl sulfate solution inside the tube for 15 minutes and discarding some. In the second test the tube was found to yield a leach rate 50% of that found for uncoated tubing. The tube was then cleaned in a no-flow situation using 0.5% sodium lauryl sulfate for 10 minutes, and then subjected to a 2 hour flex test with fresh solution. No diminution of leach rate was observed in the flex test.

However diminution of leach rate has been observed for TMDSiO glow discharge polymer in preliminary flow tests in which the tubing was not flexed. These were run by placing silastic tubing in the peristaltic pump and closing the loop with Tygon tubing.

2.3 University of Missouri-Rolla Studies of Tetramethyldisiloxane Glow Discharge Polymerization and Tetrafluoroethylene Glow Discharge Polymerization

2.3.1 Tetramethyldisiloxane Glow Discharge Polymerization

TMDSiO glow discharge polymerizations were carried out at a flow rate of 0.04 cm^3/min using the standard reactor used in procedure 1 (Table V) at RTI. The flow rate was an order of magnitude less than that used at RTI or that used in former years to coat samples for testing of blood compatibility. It did permit the evaluation of the effect of very high power to flow rate ratios on the chemistry of TMDSiO glow discharge polymer. This was done by means of infrared spectra from glow discharge polymer deposited on KBr powder, which was subsequently pressed into pellets and examined using an infrared spectrometer and the conventional transmission technique. Spectra obtained in this manner for monomer and polymer are shown in Figure 52. The effect of increasing power on the ratio of absorbance of various peaks (peak height ratios) to that of the peak at 1050 cm^{-1} (Si-O-Si) is given in Figure 53. It may be noted that increasing the power to flow rate ratio results in an increasingly methyl group poor polymer. The reproducibility for glow
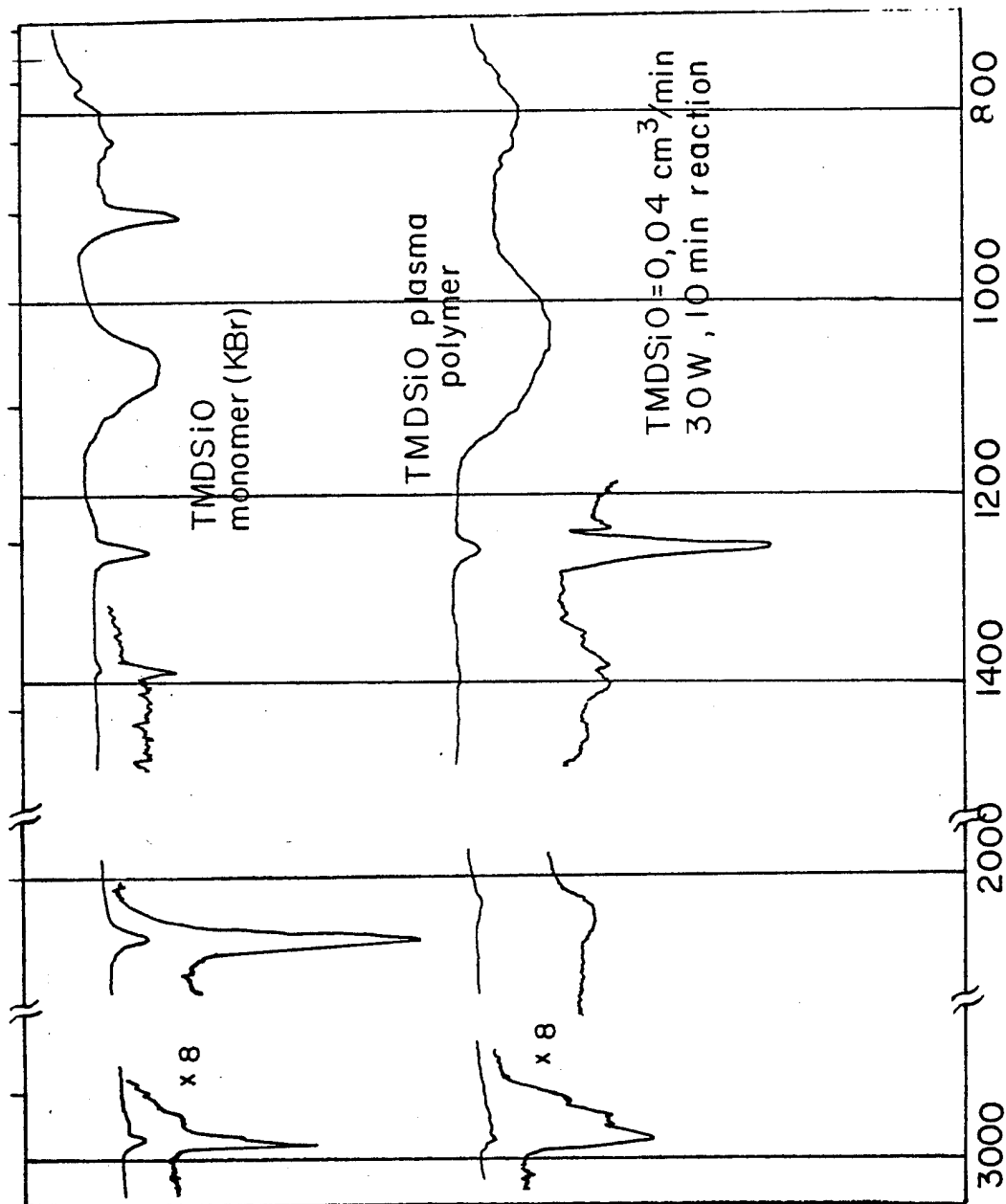
Figure 52.   Infrared transmission spectra for tetramethyldisiloxane monomer and for glow discharge polymer deposited on KBr which was subsequently pressed into a pellet.
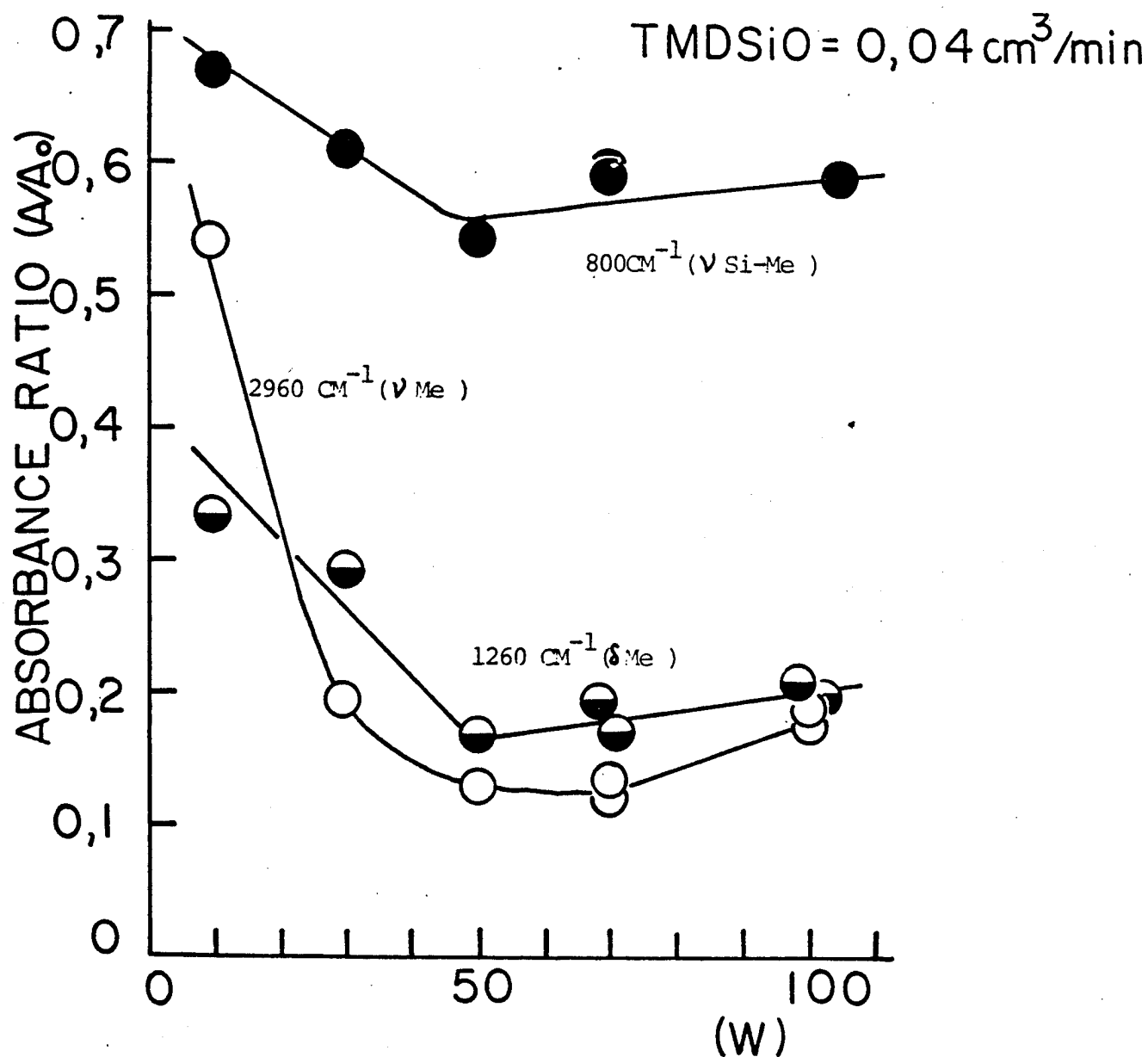
Figure 53. Peak height ratios for tetramethyl disiloxane glow discharge polymer deposited at a constant flow rate [0.04 cm^3(S.T.P.)/min] as a function of applied rf power. All peak heights are divided by that of the 1030 cm^{-1} peak in the infrared absorbance spectra.

discharge polymerization at 30W, a region particularly sensitive to change in the power to flow rate ratio (as seen in Figure 53) is shown in Figure 54.

An accelerated aging test was run on TMDSiO glow discharge polymer by incorporating it in a KBr pellet which was heated at 70°C for several months. Figure 55 shows that the peaks for Si-H disappears after 3.5 months and the peaks indicating the presence of methyl groups in Si-CH$_3$ all decrease with respect to the Si-O-Si group by at least 10% for an eight month period.

2.3.2 Tetrafluroethylene Glow Discharge Polymerization

2.3.2.1 Reproducibility

Tetrafluoroethylene (TFE) inhibited with 1-2% d-limonene was obtained from PCR Chemicals, Inc. of Gainesville, Florida. Reproducibility of TFE glow discharge polymerization is demonstrated by infrared spectra obtained for replicate preparations of glow discharge polymer under the conditions shown in Figure 56, together with the infrared spectra. The TFE polymer was deposited on NaCl powder, subsequently pressed into an IR pellet. The assignments for the peaks is given in Table XIII. A good many of the peaks (800, 730, 520, 498 and 470 cm^{-1}) appear to originate in Na$_2$SiF$_6$ band formed on etching of the glass surface of the reactor by fluorine ions. It may be noted that perfluorinated hydrocarbons are used for etching in the microelectronics industry.[127] The nature of the polymer does not appear to be very greatly affected by the use of a clean reactor (baked tube) as opposed to the use of a reactor in which prior deposition of the TFE glow discharge polymer had occurred.

Reproducibility were also obtained from ESCA spectra. The average F/C and O/C ratios obtained together with number of determinations and standard deviations are given in Table XIV. The individual determinations are presented as a function of distance from the inlet tube in the standard reactor in Figure 57. It is seen that the F/C ratio deposited on glass differs significantly from that deposited on aluminum. This may be related to reaction of fluorine with Al in the aluminum foil. ESCA signals for Al and Si were not obtained. The variation of deposition rate with position is shown in Figure 58.

The ESCA C$_{1s}$ spectra were deconvoluted according to the method described by Pavlath and Pittman[128] and by D. T. Clark et al.[129] The composition of the peak for replicate preparations at a position 20 cm
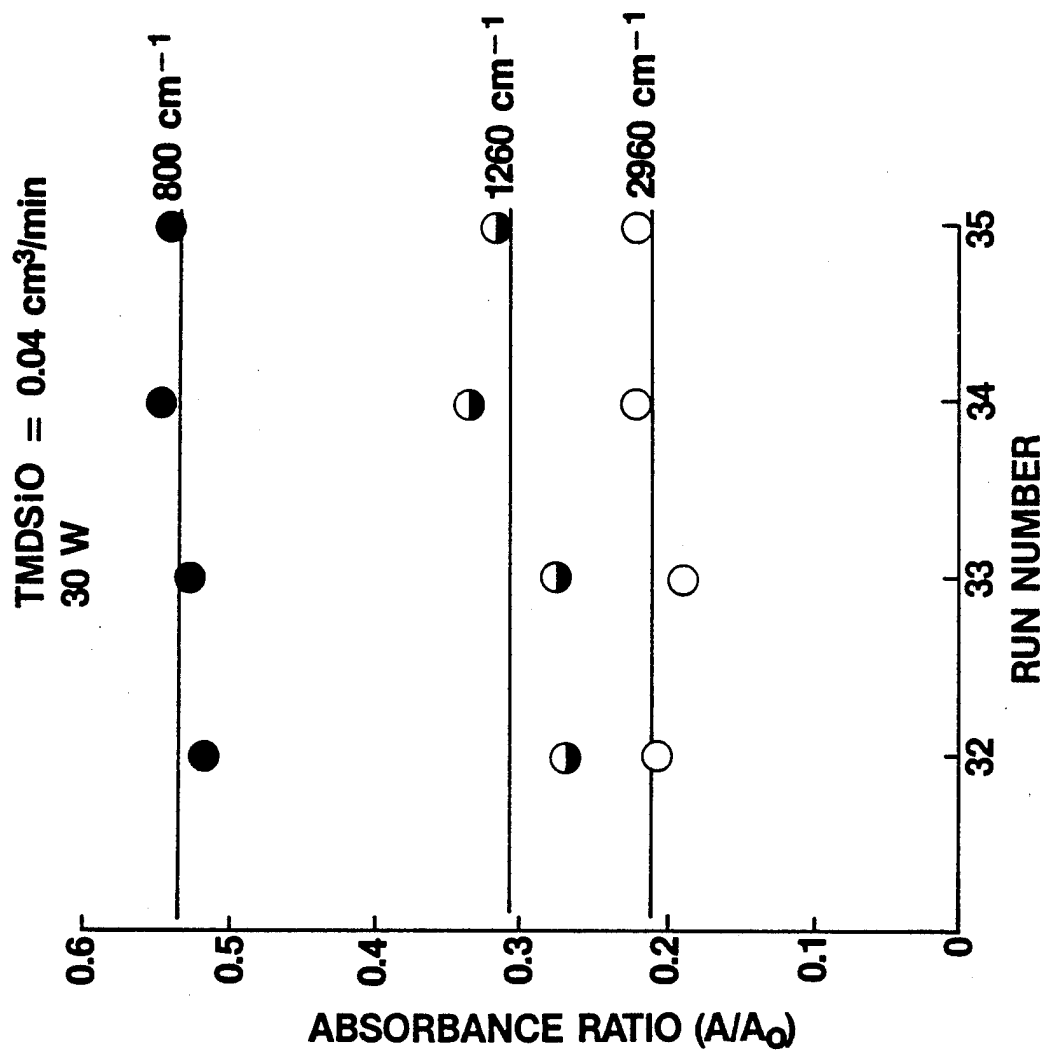
Figure 54. Infrared absorbance peak height ratios for replicate preparations of tetramethyldisiloxane glow discharge polymer prepared in standard reactor at F = 0.04 cm^3/min and 30 Watts power.
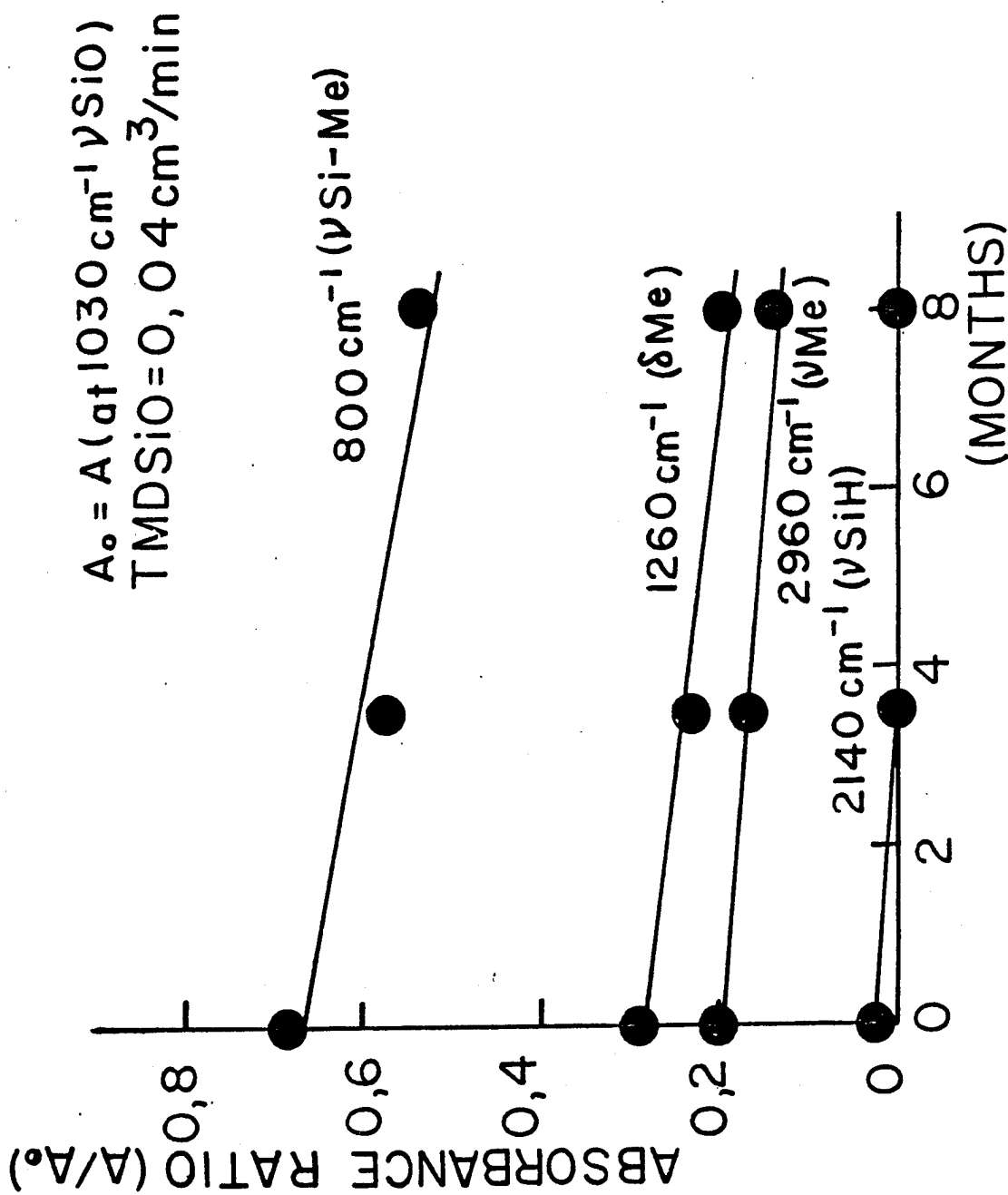
Figure 55. Infrared absorbance peak height ratios for tetramethyldisiloxane glow discharge polymer as a function of aging time at 70°C in KBr pellet.

119
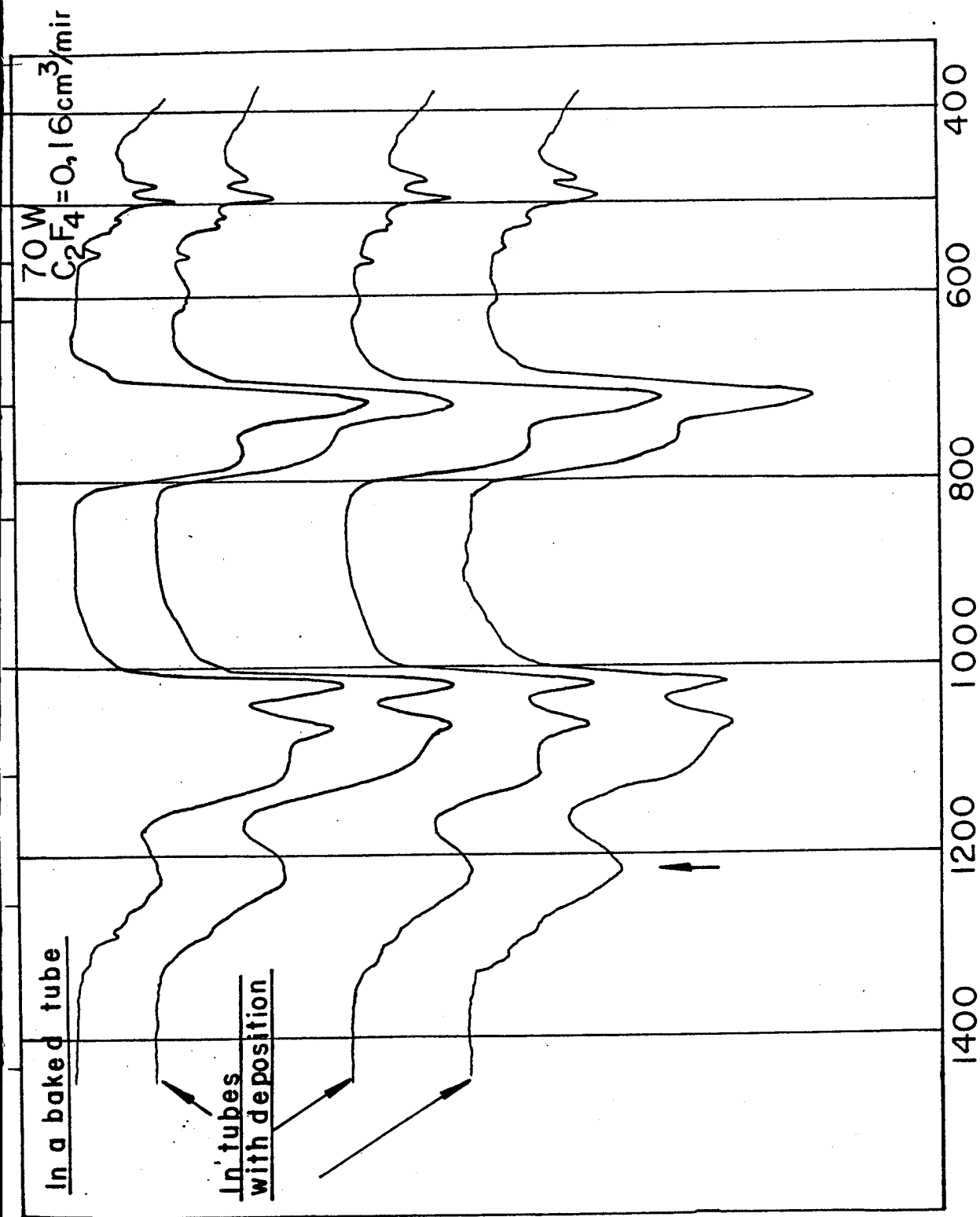
Figure 56. Infrared transmission spectra for replicate preparations of tetrafluoroethylene glow discharge polymer.
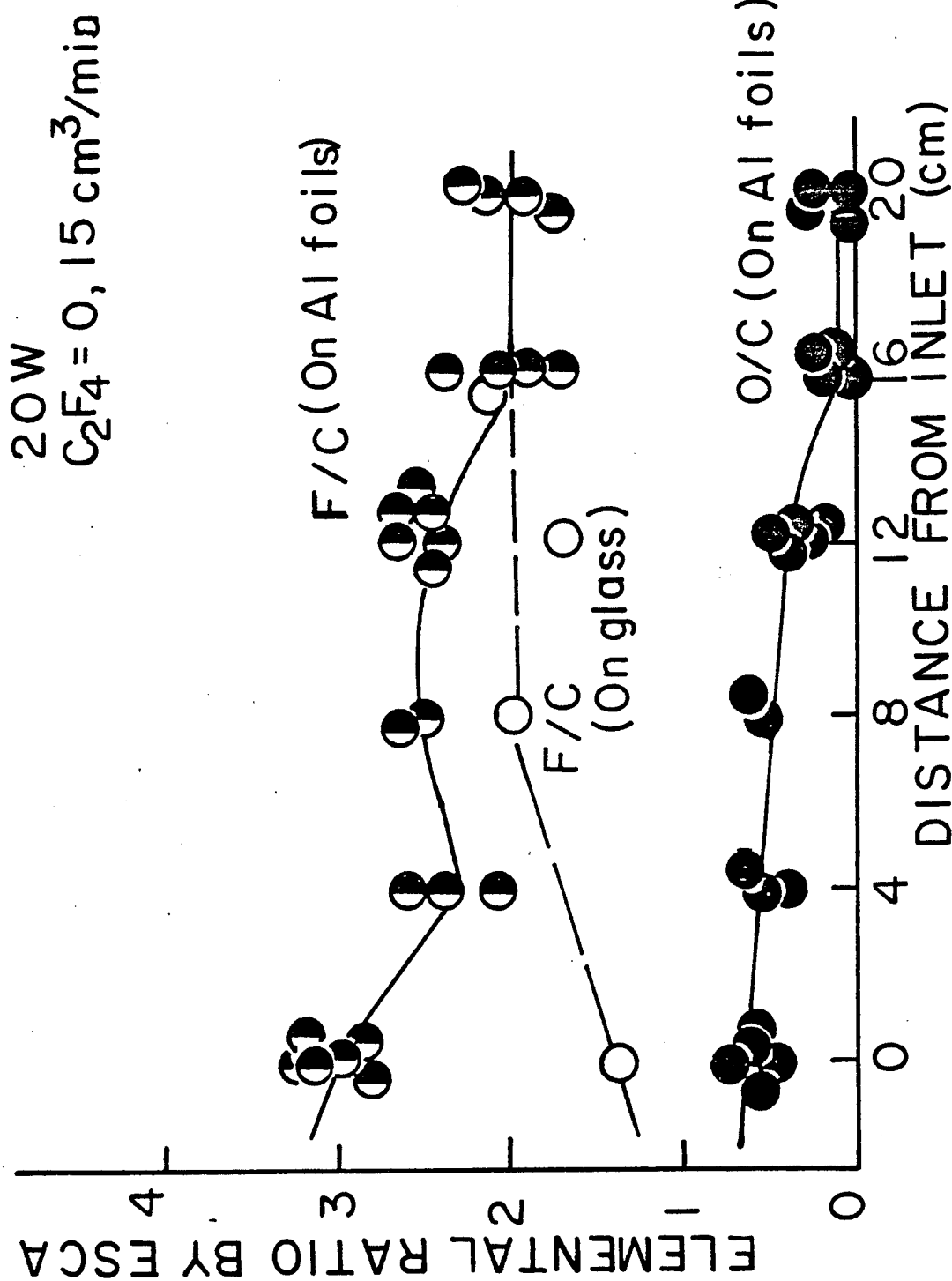
Figure 57. Elemental ratio, as obtained by ESCA, as a function of position in the standard reactor for replicate preparations of tetrafluoroethylene glow discharge polymer under constant power, constant flow rate conditions. Replicates represent sample prepared at different times.
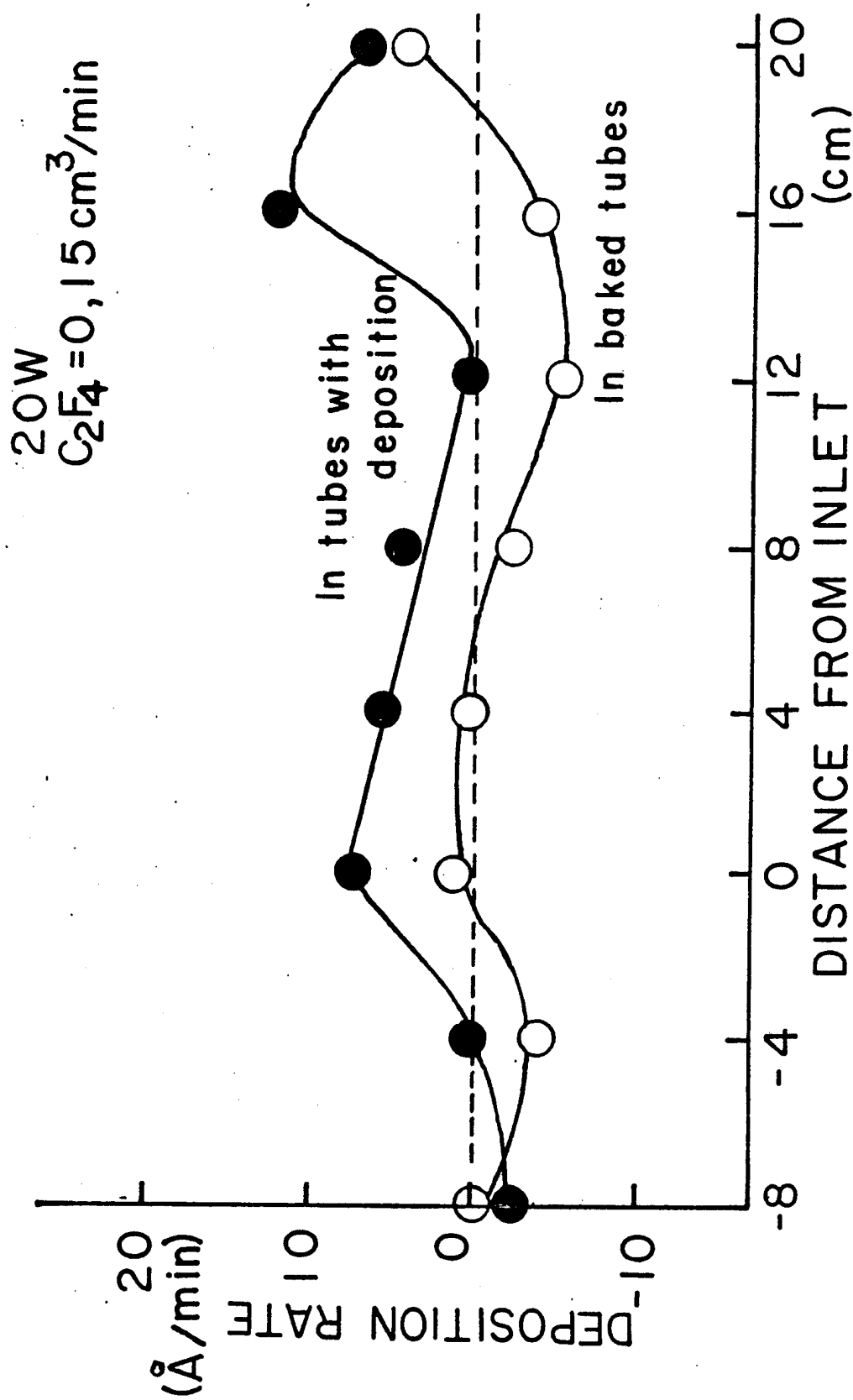
Figure 58. Deposition rate as a function of position within the standard reactor.

from the monomer inlet and low power to flow rate ratio are given in Figure 59. Both the power and position are such as to encourage the deposition of a fluorine rich polymer which is the observed result.

2.3.2.2 Effect of Power to Flow Rate Ratio

The overall effect of power to flow rate ratio is shown in the variation of pressure in the glow discharge with increasing power (Figure 60) under conditions of constant feed rate and pumping rate. The drop in pressure on application of rf power for low power levels shows that polymer deposition predominates. At higher powers, the pressure increases on application of rf power as gaseous species increase, with more fluorine in the gaseous byproducts of the reaction and less in the glow discharge polymer.

The effect of the power to flow rate ratio on IR absorbance is shown in Figure 61 and 62. In Figure 61 the IR spectra are shown for increasing powers for a fixed TFE flow rate. In Figure 62 the infrared spectra for increasing flow rate at a constant power input of 70 Watts is shown. The intensity of the SiF_6 peaks appears to be most affected by the power input and relatively unaffected by flow rate. The nature of the glow discharge polymer from TFE is affected by the power to flow rate ratio with a spectrum typical of fluorinated ethylene propylene polymer observed at low W/FM but disappearing at high W/FM.

The ESCA C_{1s} peak for polymer deposited at a position 20 cm from the monomer inlet has been deconvoluted for various input powers at a constant TFE flow rate of 0.155 cm^3/min with the results shown in Figure 63. The expected drop in the proportion of the most fluorine rich groups and rise in the proportion of the most fluorine poor groups has been observed but the effect is not great. This is because the position of deposition is very far from the rf coil. A greater effect would be expected at positions closer to the monomer inlet (and rf coil).

2.3.3 Biological Testing of Glow Discharge Polymers

Glow discharge polymers have been prepared for biological testing at the University of Missouri-Rolla for the most part. These samples included:

1. High power tetrafluoroethylene glow discharge polymer (TFE-2) coated on a silastic substrate and shipped to Prof. J. S. Schultz at the University of Michigan.
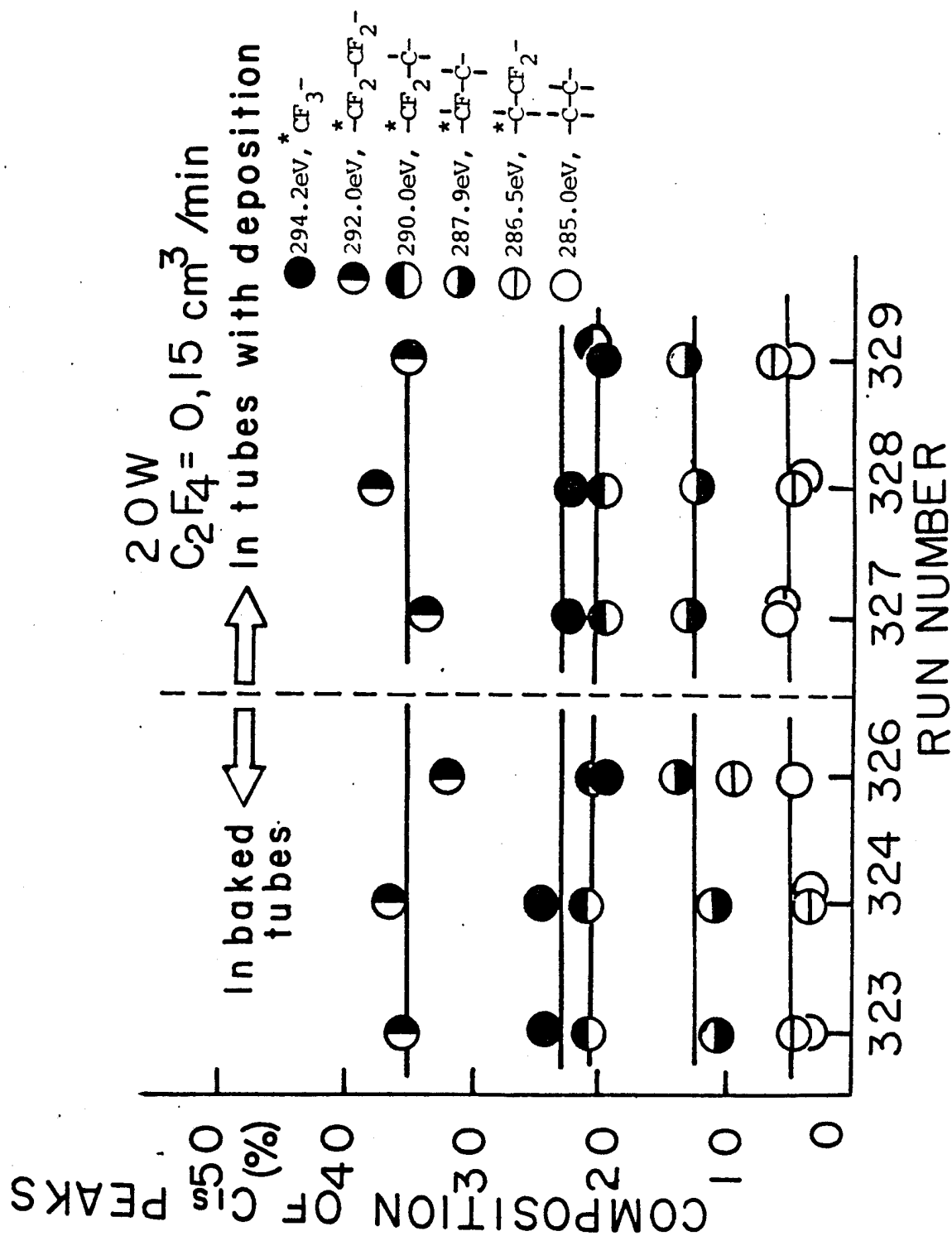
Figure 59. Composition of replicate preparations of tetrafluoroethylene glow discharge polymer as obtained by deconvolution of C_{1s} ESCA peak.
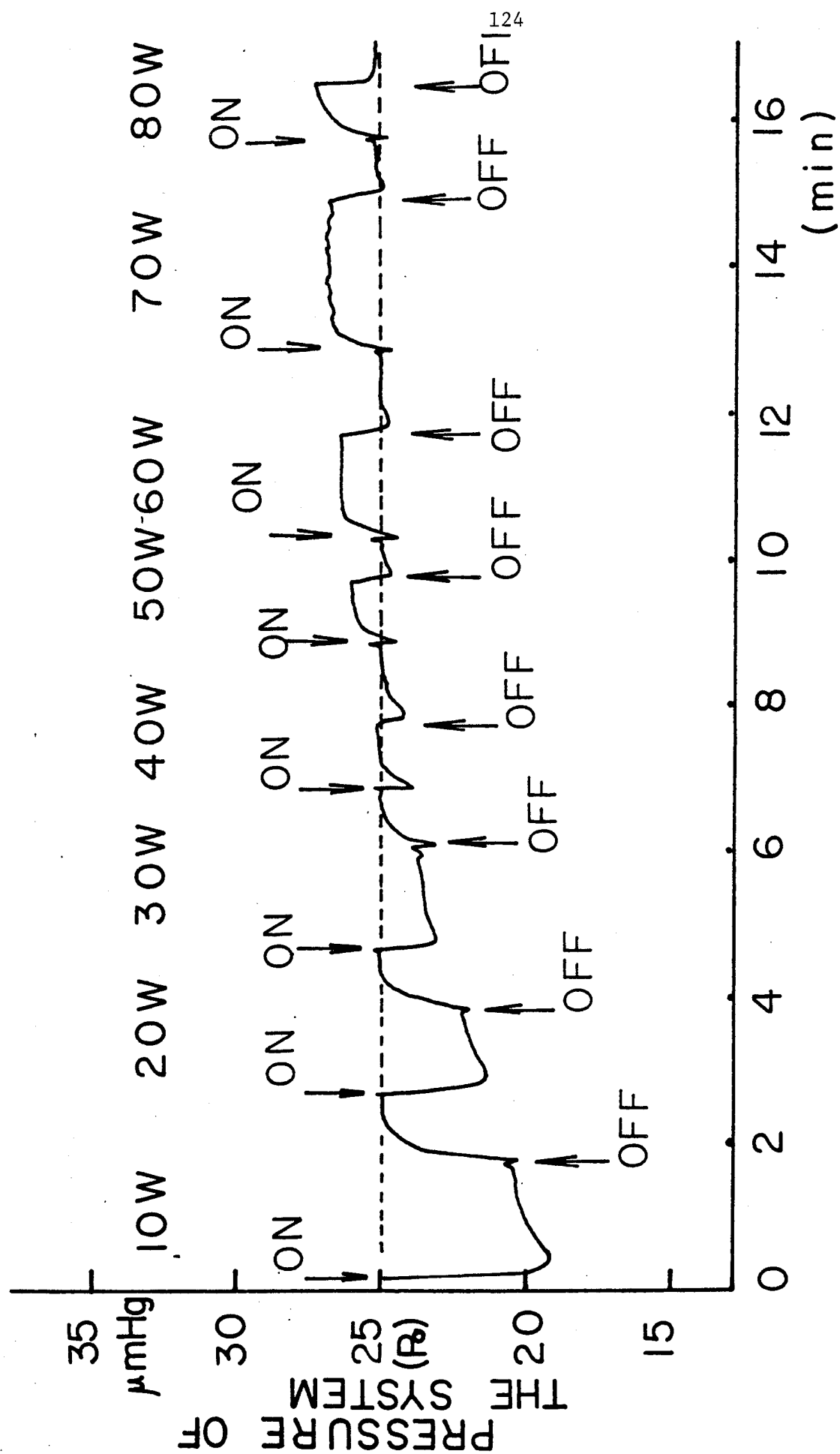
Figure 60. Pressure in the standard reactor as a function of rf power for the glow discharge polymerization of tetrafluoroethylene at a flow rate of 0.15 cm^3 (S.T.F.)/min.

Table XIII. List of IR Absorption Bands of Polytetrafluoroethylene.

Wavenumber	Assignments	Intensity & Other Characters
1545		vw
1450		w
1410		vw
1207	CF stretching	VS, asymmetric
1152	CF stretching	VS, symmetric
780		m
742		m
720		m
636	CF_2 deformation	s
620		s, shoulder
553	CF_2 deformation	s
520	CF_2 rocking	s

Poly(vinylidene fluoride) shows CF stretching bands at 1382(m), 1292(2), 1213(S) and 1182(S). Poly(vinyl fluoride) has a band at 1080 (s), which contains three components (1130, 1080, 1020 -- approximately). These bands appearing on PVF spectrum are very similar to the bands that were observed on plasma polymer spectra sampled under higher wattage conditions.
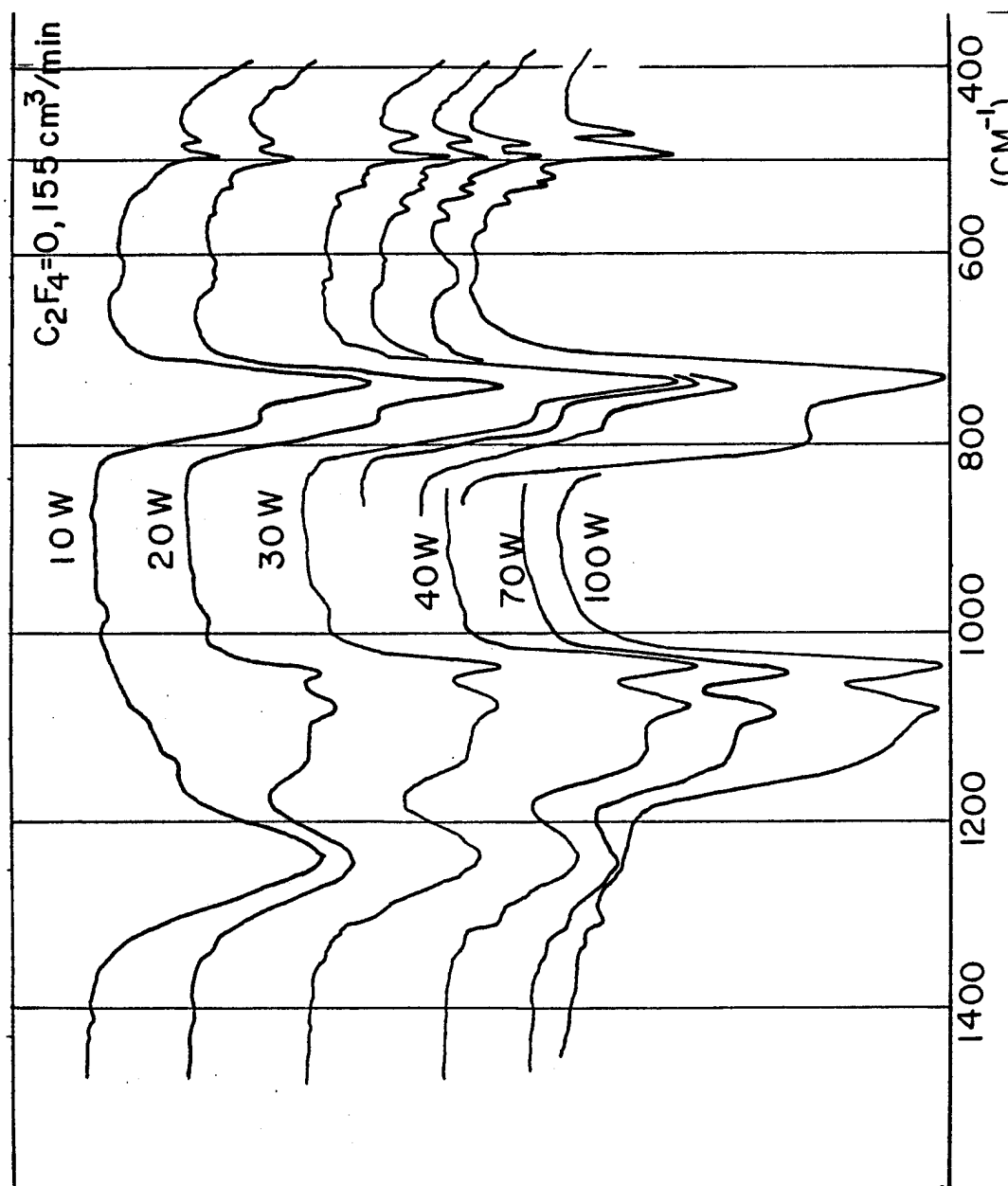
Figure 61. Infrared transmission spectra obtained for tetrafluoroethylene glow discharge polymer for fixed flow rate [0.155 cm^3 (S.T.P.)/min] but for a variety of rf power inputs.
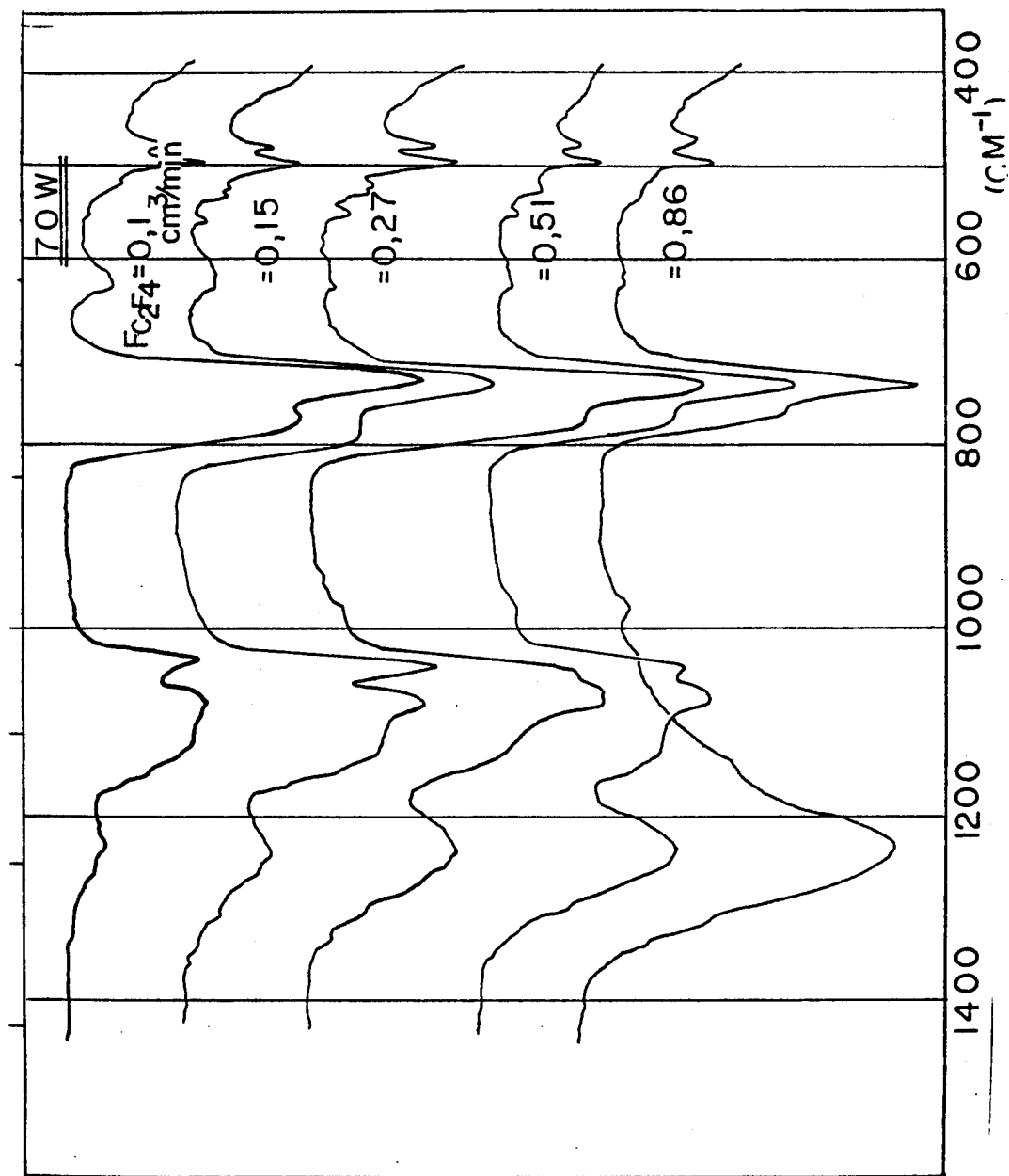
Figure 62. Infrared transmission spectra obtained for tetrafluoroethylene glow discharge polymer for fixed power (70W) for a variety of flow rates.

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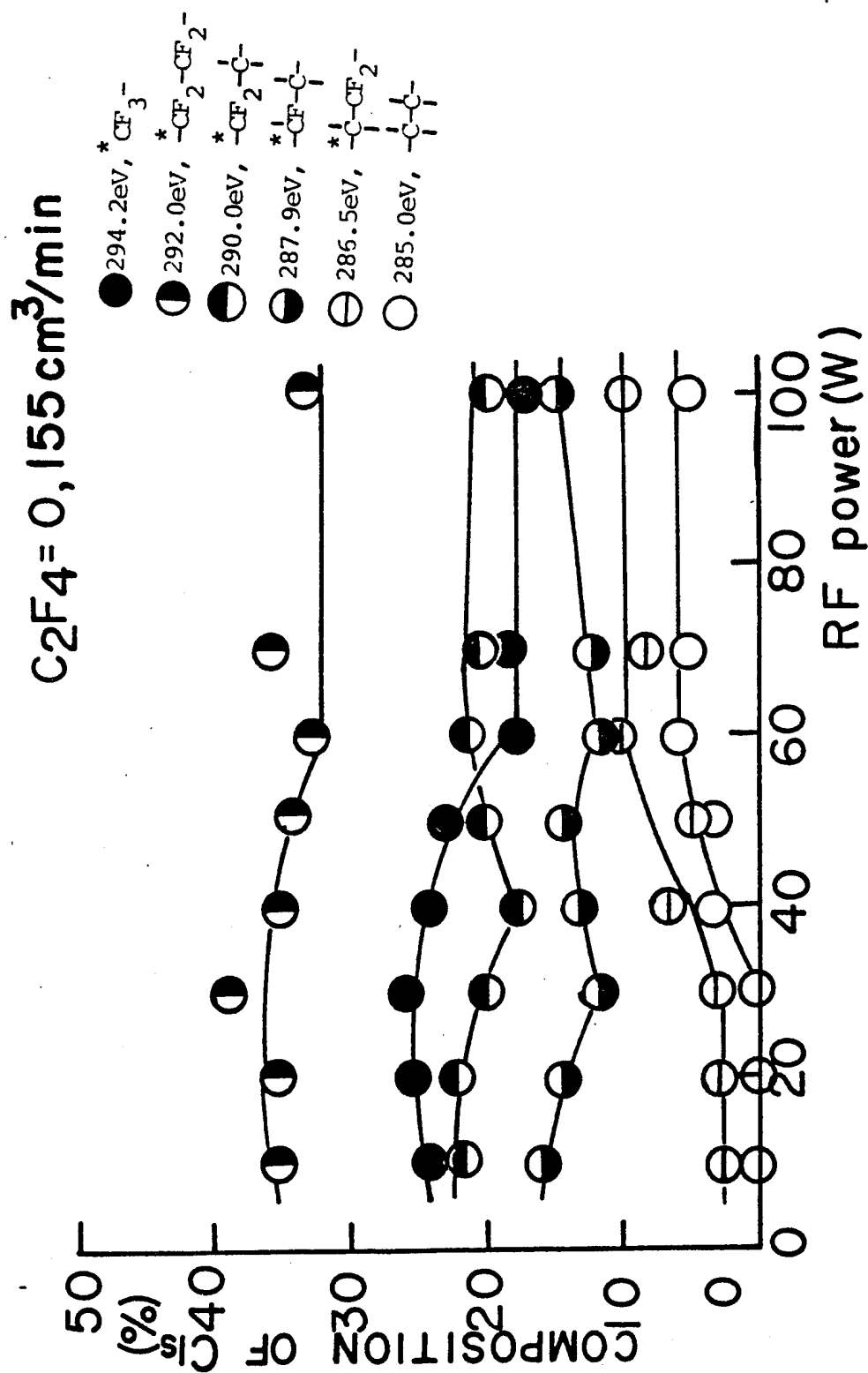
Figure 63. Composition of tetrafluoroethylene glow discharge polymer deposited at a position 20 cm from monomer inlet as a function of power, as obtained from deconvolution of C_{1s} ESCA peak.

2. Tetramethyldisiloxane and high power tetrafluoroethylenes (TFE-2) glow discharge polymers deposited on glass and shipped to Dr. E. Nyilas at Avco Everett Research Labs.

3. Tetramethyldisiloxane glow discharge polymer deposited on small $(0.5 \text{ cm})^2$ PVC pieces using a rotating drum insert in the standard reactor. Conditions of glow discharge polymerization were as described in Section 2.3.1. Two batches of such samples were prepared. For one batch an argon glow discharge treatment preceded the glow discharge polymerization. For another, only the coating with glow discharge polymer was carried out. The samples were sent to Dr. John Autian at the University of Tennessee for toxicology testing.

   All samples prepared at the University of Missouri were introduced into the reactor and removed in a clean room. Samples described under 1 and 2 above, were then placed in sterilization bags and sterilized using ethylene oxide gas.

4. Additional samples were prepared at RTI and sent to the University of Tennessee for toxicology testing. These included:

   a) Samples for muscle implant tests (1 cm x 1 mm)
      i)   Poly(vinyl chloride) controls (PVC)
      ii) Polyethylene controls (PE)
      iii) PVC coated with 800-1600 $\overset{o}{A}$ of TMDSiO glow discharge polymer (procedure 1, Table V)
      iv) PVC argon glow discharge treated, then coated with 800-1600 $\overset{o}{A}$ of TMDSiO glow discharge polymer. [The argon glow discharge treatment was carried out in the standard reactor, $F = 0.12 \text{ cm}^3$ (STP)/min, Power = 70 Watts, $P_o = 11$ mTorr, $P_g = 25$ mTorr, duration of treatment = 6-12 minutes].
      v)   PE coated with 800-1600 $\overset{o}{A}$ TMDSiO glow discharge polymer.

   b) Samples for Agar overlay tissue culture assays (1 cm x 1 cm) (i-v above)

   c) Samples for extraction (1/2 cm x 1/2 cm)
      i, ii in (a)
      iii, iv in (a) were prepared at University of Missouri (Item 3 above)

5. Descriptions of some of the tests mentioned above and results for
previous years can be found in the reports numbered NIH-NO1-HV-4-2961-3
(Avco-Everett) and NIH-NO1-4-2962-4 (U. Mich.). Work at the University
of Tennessee was carried out under contract No. NIH-NO1-HV-82914 and the
reports would bear this number.

2.4 Discussion

In previous years we have shown that the character of the glow
discharge polymer deposited depended not only on the monomer but also on
such operational parameters as the design of the glow discharge reactor,
the power to flow rate ratio, the location of glow discharge polymeriza-
tion with the reactor, etc. On the one hand this has made possible a
variation of chemical and physical properties for glow discharge polymers
in a continuous fashion, rather than the step-wise fashion inherent in
the chemistry of conventional stoichiometric materials. On the other,
it has apparently left the impression among non-practioners in the field
that the reproducibility of the process is not good. In the last year
of the contract we have shown, by infrared absorption spectrometry and
ESCA techniques that when care is taken to keep the conditions of glow
discharge polymerization constant, excellent reproducibility can be
attained. Perhaps the best demonstration of this is found in the FTIR
work at RTI for TMDSiO glow discharge polymer deposited in the straight
tube reactor. Here, for conditions where errors in the evaluation of
the infrared spectra are minimized, a standard deviation of 6% or better
is obtained for peak area ratios obtained for replicate preparations of
glow discharge polymer (see Table VIII). Similar results are obtained
for elemental ratios (from ESCA spectra taken on the day that the glow
discharge polymer was prepared). Here all elemental ratios agree within
a standard deviation of 10% or better for replicate preparations (Table
IX and X).

An important aspect of the RTI work is that it was carried out on
glow discharge polymer deposited under conditions identical to that used
to coat PVC tubing (for barrier property studies) or PVC sheet (for
toxicology studies at the University of Tennessee). The thickness of
the deposited layer was also identical. The most thorough analysis of
reproducibility data was carried out for tetramethyldisiloxane glow

discharge polymer deposited under the conditions of procedure 2 in Table V (using the straight tube reactor). However, reproducibility data was also obtained for two preparation methods using the standard reactor, one set of data at RTI and another at the University of Missouri. These indicate that good reproducibility can be obtained using the standard reactor as well. Intuitively one would expect that it should be easier to reproduce results using the standard reactor than with the straight tube reactor, but not enough data was collected under identical conditions of analysis to verify this. We conclude that although we have produced three different tetramethyldisiloxane glow discharge polymers under three different sets of conditions, we can reproduce any one of these polymers rather well.

The study of aging of tetramethyldisiloxane glow discharge polymer has uncovered two phenomena, one dealing with the ratio of $Si(CH_3)$, $Si(CH_3)_2$ and $Si(CH_3)_3$ groups. Information concerning these three groups was not available to us previously.

Firstly, the glow discharge polymer is found to increase in oxygen content with time. This is seen directly from the ESCA elemental ratios and from the growth of carbonyl and Si-OH peaks in the FTIR spectra. Secondly there is a loss of Si-H, $Si(CH_3)$ and $Si(CH_3)_3$ groups (but not $Si(CH_3)_2$ groups) with time. It appears that branching may occur by the conversion of SiH to SiOH to SiOSi groups. There may be some loss of oligomers; gravimetric data as a function of aging would be useful. As the proportion of SiH, and of $Si(CH_3)$ and $Si(CH_3)_3$ groups can be controlled by the reaction conditions, it is possible to make a tetramethyldisiloxane glow discharge polymer where the number of these groups are minimal, resulting in a more stable polymer.

Infrared and ESCA data were obtained for tetrafluoroethylene glow discharge polymer at the University of Missouri. The IR data revealed that Na_2SiF_6 was present along with glow discharge polymer. This species resulted from fluorine etching of the glass reaction chamber and reaction with the NaCl on which the glow discharge polymer was deposited. Reasonably good reproducibility was also obtained for the chemical character of the deposited glow discharge polymer. For example for positions where a large number of replications were carried out, Table XIV, reveals

Table XIV. Elemental Ratios for TFE Glow Discharge Polymer by ESCA.

Location (cm. from inlet)	F/C		O/C		Number of Replications
	Elemental Ratio	Standard Deviation	Elemental Ratio	Standard Deviation	
0	3.01	0.16	0.67	0.09	7
4	2.34	0.30	0.53	0.14	3
8	2.51	0.01	0.42	0.10	2
12	2.51	0.11	0.34	0.09	7
16	2.01	0.25	0.11	0.08	4
20	1.98	0.20	0.12	0.14	4

F/C ratios with standard deviations of better than 10%. O/C ratios appear to be somewhat less reproducible. The problem which the investigation of TFE glow discharge polymer has revealed is that in addition to C, O and F in the glow discharge polymer, other elements are also present due to the etching ability of the fluorine containing glow discharge. Thus hindsight shows that the ESCA investigation should have included a search for a Si peak. As the glow discharge polymer was deposited on Al, Al was found on the surface. The choice of substrate was found to affect elemental ratios. In future studies, this aspect should be kept in mind. Additionally the analysis of the glow discharge polymer should be made as nearly as possible on polymer deposited under the same conditions, as the conditions of use. $\underline{E.g.}$, if 1000 $\overset{\circ}{A}$ of a fluorine containing glow discharge polymer is to be deposited on a polypropylene substrate for blood compatibility testing, the chemical characterization should be of 1000 $\overset{\circ}{A}$ of the polymer deposited on a polypropylene (not aluminum) substrate.

Glow discharge treatment of poly(vinyl chloride) tubing has been shown to form a barrier layer on the surface of the tubing which inhibits leaching of dioctyl phthalate plasticizer from the tubing. In a severe flex test using a peristaltic pump, the leach rate was reduced to as low as 30% of that for untreated tubing. For a non-flow test involving no bending or flexing of the tubes (e.g., as would be expected for a blood bag) the leach rate was reduced to as little as 5% of that for untreated tubing. The argon glow discharge treatment is carried out using a stationary coil, but some data has been obtained using a coil moving over the tubing which suggests that comparable results could be obtained in this way as well. This would allow treating an "infinite" length of tubing.

The glow discharge treatment forms a crosslinked layer on the surface of the tubing as shown by its insolubility in tetrahydrofuran. Cracks are formed in the crosslinked layer during flexing but are of less than 1 μm width.

Tetramethyldisiloxane glow discharge polymer was much less effective in inhibiting leaching although a reduction to 30% of untreated leach rate was found in a non-flow test. It may be pointed out, however, that

a variety of glow discharge monomers would be expected to yield better barrier properties than tetramethyldisiloxane glow discharge polymer. These could be subsequently coated with tetramethyldisiloxane glow discharge polymer yielding a sandwich structure with both good barrier properties and blood compatibility.

3.0 Conclusions

This contract has been concerned with exploring the potential of modifying the surface of conventional polymers by using an electrodeless glow discharge. Two methods of surface modification have been used. In glow discharge treatment the surface of the substrate is chemically altered by the glow discharge. In glow discharge polymerization, the surface is coated with a highly crosslinked polymer deposited from, and reacting with components of, the glow discharge. The bulk of the work has been concerned with the latter process.

In developing the glow discharge polymerization technique, we have carried out an extensive survey of the relation between the chemical nature of the glow discharge polymer on the monomer feed, as well as operational parameters such as power, flow rate, pressure and geometry of the reactor. A complete discussion of this survey is given in Section 1.0 of this report.

From the point of view of using glow discharge polymers as coatings for use in prosthetic devices, the following characteristics are relevant:

1. Excellent bonding of the glow discharge polymer to the substrate polymer.

2. Glow discharge polymer forms a flexible, infusible, insoluble ultrathin coating.

3. Modification of the surface occurs without affecting the bulk properties of the substrate.

4. The surface properties of the coating are those inherent in the plasma polymer and are generally not affected by the substrate. Exceptions to this include substrates which contain volatile materials or monomers which are also strong etchants (e.g., fluorinated compounds).

5. Promising blood compatibility is indicated by tests performed on these surfaces by other contractors.

6. The coating imparts abrasion resistance.

7. The physical and chemical nature of the plasma polymer coating are controlled by choice of monomer(s) and of plasma polymerization conditions. Thus surfaces with a wide range of chemical properties are accessible by this technique.

In the last year of the contract, excellent reproducibility of the chemical nature of glow discharge polymers has been shown to be possible based on an appreciation of the effect of operational parameters. The leaching of plasticizer from PVC has also been inhibited by glow discharge treatment. These aspects are covered in Section 2.0 of this report.

Some comments on the blood compatibility of glow discharge polymers may be made based on the reports of other contractors who have tested these materials and their informal comments.

A large number of glow discharge polymer coated samples were sent to Dr. Yates at Utah Biomedical Laboratory. These samples were the only ones received by Dr. Yates in a number of sufficient for statistical handling of the data. Whereas materials prepared by other investigators generally covered the gamut of possible results for any one material, the glow discharge polymer coated samples using fluorinated ethylene or ethane showed very few occlusions after 2 hours; of those samples implanted for 2 weeks an unually large number were patent at the end of the experiment. Glow discharge polymers using tetramethyldisiloxane and fluorinated monomers were tested by Dr. Yates.

Tetramethyldisiloxane and acetylene + N_2 glow discharge polymer coatings were made on rings sent to Dr. Kusserow of the University of Vermont. A limited number of samples were prepared and tested but these compared favorably with those received from other investigators.

Tetramethyldisiloxane glow discharge polymer was deposited on stainless steel shafts and sent to Dr. J. Schultz at the University of Michigan. It was found that the polymer deposited directly on the stainless steel adhered poorly and for this reason a second set of samples was prepared where the coating was deposited on siloxane coated stainless steel shafts. This second set of samples scored near the top of Dr. Schultz's rating system for all samples tested.

Samples sent to Dr. Nyilas at Avco Everett were tested and the results statistically treated. It was found that the glow discharge polymer coated samples were more consistent than the blank.

Thus the method produces blood compatible surfaces that are very clean and free of impurities. In this respect it is superior to other methods of modifying surfaces. The fact that properties can be varied

continuously over a wide range due to control both by choice of monomer and by control of operational parameters suggests that until now we have merely spot checked the behavior of a few of the infinite number of glow discharge polymers. Systematic variation of their properties and more reliable biological testing protocols may yet lead to the ideal glow discharge polymer coating for prosthetic devices in contact with human blood.

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